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Sensory, rheology, tribology and shelflife of reduced fat mayonnaise-type emulsions formulated with lipid-modified maize starch as fat replacer

By

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Declaration

I declare that the thesis, which I hereby submit for the degree PhD (Food Science) at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution

Joyce Agyei-Amponsah (Mrs)

Date: ………………….

Dedication

To my husband for his love and encouragement

Alex, you are always there for me and the kids. On countless occasions you single handedly made hospital trips at night with our young ones all in support of my studies. Your overwhelming emotional support cannot go unnoticed. God bless you.

Love, Naana

To my children, Oseiwaa and Paapa

Mummy left you to pursue her PhD degree when you barely understood the importance of schooling. This is dedicated to both of you, for your love, support, understanding and good behaviour while I was away.

Mmmwah!!! to both of you

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Singing, "Amen! Blessing and glory and wisdom and thanksgiving and honour and power and might be to our God forever and ever! Amen." **(**Revelation 7:12)

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Abstract

Sensory, rheology, tribology and shelf life of reduced-fat mayonnaise-type emulsions formulated with lipid-modified maize starch as fat replacer

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Joyce Agyei-Amponsah

Supervisor: Prof. M.N. Emmambux

Co-Supervisor: Prof. H. L. DeKock

The increasing rate of obesity and its related diseases (cancers, heart disease and diabetes) has become a global health issue. Dietary fat is highlighted as one of the critical risk factors contributing to this problem. Reduction of the fat content of popular food products, in an attempt to reduce fat intake without compromising the desirable sensory properties provided by fat, is challenging. This study characterised two lipid-modified maize starches (maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride) produced by incorporating food-friendly lipids into maize starch through wet-heat processing. Sunflower oil was substituted with these complexes in the production of reduced-fat mayonnaise-type emulsions, at 0 % (control), 50 %, 80 % and 98 % oil replacement, with qualities similar to that of full-fat mayonnaise. The effect of the substitution on the rheological, lubricating, descriptive sensory profile (panel, n =10), consumer acceptance (consumers, n = 207), and accelerated shelf-life (40 °C with 24 h UV illumination) of the reduced-fat mayonnaise-type emulsions was determined.

The lipid-modified starches were non-gelling, glossy, smooth, creamy, easy-to-swallow and had good lubricating properties. These attributes could be ascribed to the formation of amylose-lipid complexes during the modification process of maize starch with stearic acid and monoglyceride. The formation of amylose-lipid complexes prevented further aggregation of amylose double helixes from forming crystalline structures and made amylose less available for junction zone formation and molecular entanglement, resulting in non-gelling starches. The lower friction coefficient values recorded for the starch-lipid complexes could be due to the nanoparticle sizes (2.4–6.7 nm) of the amylose-lipid complexes. The nanoparticle nature of the amylose-lipid complexes possibly increased the volume to surface area ratio of the complexes making them

more available to act as a layer of lubricant. Lower friction coefficient implies increased lubricating effect, which enhances the sensory perception of fat-related attributes, thus influencing the perceived smoothness, creaminess, and easy-to-swallow nature of the starch-lipid complexes.

All the reduced-fat mayonnaise-type emulsions were smooth, melting, and easy-to-swallow and the starch/monoglyceride emulsions had a higher thickness, creaminess and mouth-coating. The higher thickness and mouth-coating can be attributed to the availability of uncomplexed amylose, which is more abundant in the starch/monoglyceride fat-replacer than in starch/stearic acid one, to form junction zones and molecular entanglements. The amylose-lipid complexes present in the fat replacers provided the emulsions with a non-gelling highly viscous matrix that stabilised the residual oil droplets in the reduced-fat mayonnaise-type emulsions. All the reduced-fat mayonnaise-type emulsions showed good lubrication with starch/monoglyceride emulsions showing more sensitivity to coalescence and gave rise to lower friction than starch/stearic acid emulsions.

The lipid-modified starches did not effectively retard the rate of lipid oxidation in the reduced-fat mayonnaise-type emulsions at accelerated storage. Hence the oil droplets could easily interact with the aqueous phase pro-oxidants, thus increasing the rate of oxidation. The possible increase rate of oxidation could also be due to the presence of liberated iron ions, Fe^{2+}, from the egg yolk present as a stabiliser in the aqueous phase at the lower pH (< 4). At 50 % probability of consumer acceptance, the reduced-fat mayonnaise-type emulsion containing 80 % starch/monoglyceride was the most acceptable and had a predicted accelerated shelf-life beyond the 35 storage days.

The study has demonstrated the effective use of the two novel fat replacers to replace up to 80 % sunflower oil in the production of reduced-fat mayonnaise-type emulsions without compromising the desirable in-mouth textural properties of smoothness, creaminess, melting and mouth-coating. These fat replacers can be produced on a large scale and used as ingredients in commercial applications to improve the in-mouth textural properties of reduced-fat foods.

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1.0 INTRODUCTION

1.1. Problem statement

Dietary fat has been highlighted as one of the critical risk factors that contribute to several non-communicable diseases, such as obesity, cardiovascular diseases, type 2 diabetes, and cancer (Siri-Tarino, Sun, Hu & Krauss, 2010; Vorster, Badham & Venter, 2013; Mozaffarian, 2016). Urbanisation and the pursuit of convenient foods have shifted dietary preferences from nutrient-dense towards energy-dense foods characterised as high fat, refined carbohydrates and low–fibre (WHO, 2003; Kearney, 2010). In 2016, about 1.9 billion adults above 18 years and 41 million children under the age of 5 were either overweight or obese (WHO factsheet, 2018). In Africa alone, the number of overweight children under 5 has increased by nearly 50 % since 2000. In South Africa, more than one in four of the population aged 15 years and over (about 16 % men and over 35 % of women) is obese (OECD (2017). The increasing rate of obesity and its related diseases (cancers, heart disease and diabetes) is alarming and has become a major global health challenge.

Reduction of fat content by the use of fat replacers without compromising the desirable sensory properties could contribute positively to nutrition and wellbeing. However, numerous foods formulated with fat replacers cannot be likened to their full-fat counterparts (Akoh, 1998), making it challenging for people to sustain a reduced-fat dietary regime. For instance, low-fat foods containing Inulin and oligofructose scored lower in acceptability than their full-fat counterparts, Inulin powder and Simplesse® as fat replacers produced bread slices with harder crumbs compared to the control and addition of β-glucan resulted in unfavourable appearance and colour of reduced-fat mayonnaise (Devereux, Jones, McCormack & Hunter, 2003; O'brien, Mueller, Scannell & Arendt, 2003; Worrasinchai, Suphantharika, Pinjai & Jamnong, 2006). Therefore, finding an 'ideal fat replacer' that can effectively maintain the physicochemical and sensory attributes derived from fat remains a challenge.

Fat replacers are ingredients that can be added to reduced-fat foods to provide them with some qualities of fat (Ognean, Darie & Ognean, 2006). Fat replacers are generally categorised into two groups, fat substitutes, and fat mimetics. Fat substitutes are mainly produced from lipid-based ingredients, and they chemically resemble lipids. Fat mimetics are protein or carbohydrate-based ingredients, and they imitate the sensory or physical properties of triglycerides (Akoh, 1998; Ognean *et al.*, 2006). Examples of carbohydrate-based fat mimetics are common food constituents such as starch and cellulose. These may be chemically or physically modified to mimic the function of fat. Native starches can be chemically modified to improve their functionality and diversify their usage in the food industry (BeMiller, 2011; Kaur, Ariffin, Bhat & Karim, 2012). However, concerns about consumer and environmental safety on the use of chemicals (Zia-ud-Din, Xiong & Fei, 2017), has encouraged the use of food-friendly chemicals such as stearic acid and monoglyceride, in the production of 'clean' label starches (Maphalla & Emmambux, 2016).

Amylose present in starch form complexes with ligands such as fatty acids and lipids during starch gelatinisation (Putseys, Lamberts & Delcour, 2010)). These lipids form complexes with amylose, known as amylose-lipid complexes with the hydrocarbon portion of the lipids inserted into the helical cavity of amylose (Putseys *et al*., 2010; López, de Vries & Marrink, 2012). Some desirable functionalities of starch-lipid complexes in food systems have been reported, these include; no occurrence of syneresis in yoghurt samples (Singh & Byars, 2009), reduction of the process of retrogradation during cooling and storage (D'Silva, Taylor & Emmambux, 2011), production of low-calorie mayonnaise type emulsions with higher viscosity and high-temperature stability (Teklehaimanot, Duodu & Emmambux, 2013).

Starch-lipid complexes as food additives in low-fat foods have been proposed to have the ability to increase viscosity, add flavour and improve texture (Singh & Byars, 2009). They are also non-gelling (D'Silva *et al*., 2011; Maphalla & Emmambux, 2016) and nano-particulate in size due to amylose lipid complexes (Cuthbert, Ray & Emmambux, 2017). However, little literature exists on the lubricating behaviour and sensory properties of these complexes on their own, as food ingredients providing specific product properties. Therefore, this study aims at characterising two starch-lipid complexes (maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride) and substitute sunflower oil with these complexes in the production of reduced-fat mayonnaise-type emulsions with qualities similar to that of full-fat mayonnaise.

2.0 LITERATURE REVIEW

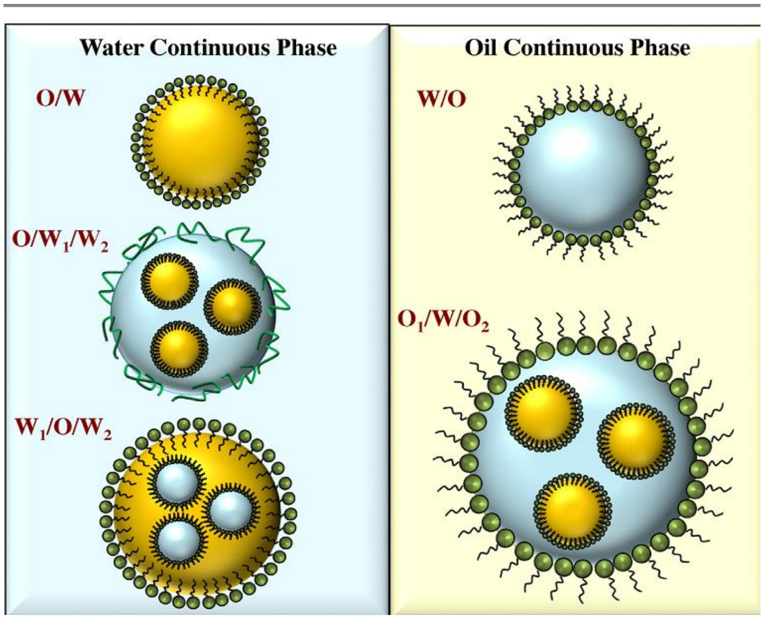
This chapter provides an overview of food emulsions, specifically mayonnaise and the functionality of the various ingredients in determining the overall emulsion quality. Focus is made on reduced-fat mayonnaise-type emulsions and the use of modified starches (lipid-modified) as fat replacers in their production. The quality characteristics of food emulsions in terms of physical, chemical and microbial stability are reviewed. Lastly, the effect of fat replacement on the quality characteristics (sensory, tribological and rheological properties) of reduced-fat mayonnaise-type emulsions are highlighted.

2.1 FOOD EMULSIONS

2.1.1 Definition and types of emulsion

An emulsion consists of two immiscible liquids (usually oil and water), with one of the liquids dispersed as small spherical droplets in the other. In foods, droplet diameter is usually in the range of 0.1 to 100 µm (Dickinson & McClements, 1995). A system which comprises of oil droplets dispersed in the aqueous phase is called an oil-in-water (o/w) emulsion (Figure 2.3). Examples of o/w emulsion foods are mayonnaise, salad dressings, milk and cream. Emulsions with water droplets dispersed in an oil phase are known as water-in-oil (w/o) emulsions (Figure 2.1), and margarine, butter, and spreads are common examples.

There is yet another kind of emulsion referred to as multiple emulsions or double emulsion. This is a mixture of water-in-oil and oil-in-water elements contained within the same system (Muschiolik, 2007; Chung & McClements, 2014). The two major types of multiple emulsions are water-in-oil-in-water ($W_1/O/W_2$) and oil-in-water-in-oil ($O_1/W/O_2$) emulsions (Figure 2.1) (Muschiolik, 2007). Multiple emulsions are used mainly in the food processing industry to encapsulate or protect sensitive and active food components from the environment, to control aroma and flavour release (Muschiolik, 2007) and to produce foods with a lower oil or fat content (Lobato-Calleros, Rodriguez, Sandoval-Castilla, Vernon-Carter & Alvarez-Ramirez, 2006).



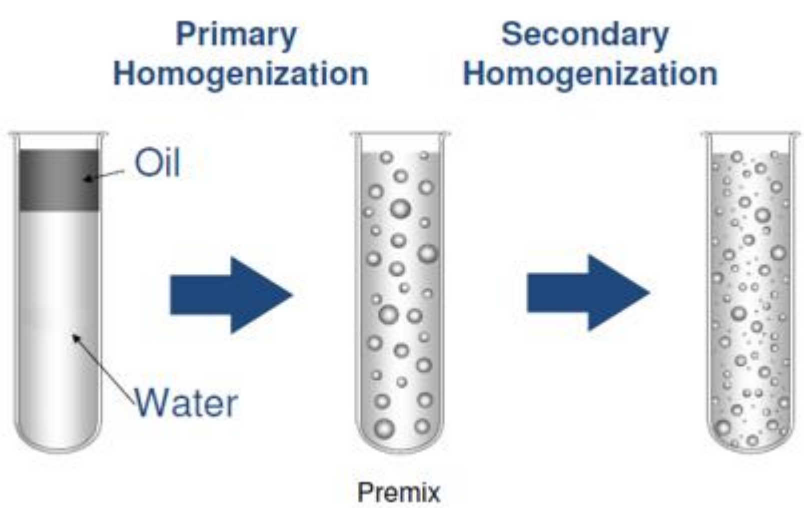
(Chung & McClements, 2014)

Figure 2.1. Schematic diagram of simple emulsions – oil-in-water (O/W) emulsion, and water-in-oil (W/O) emulsion, and multiple emulsions – oil-in-water-in-water (O/W/W) emulsion, water-in-oil-in-water (W/O/W) emulsion, and oil-in-water-in-oil (O/W/O) emulsion

2.1.2 Principle of emulsion formation

Emulsions are made up of droplets, also denoted as the dispersed, discontinuous, or internal phase, and the surrounding liquid is called the continuous or external phase. Emulsion formation involves the violent disruption of droplets and the movement of surface-active molecules from the continuous phase to the interfacial region (McClements, 2005). Final droplet formation in an emulsion utilises homogenisers that generate intense, disruptive forces capable of disrupting and vigorously mixing the oil and aqueous phases (McClements, 2012). Example of these homogenisers include high shear mixers, high-pressure valve homogenizers, microfluidisers, and sonication methods (Stang, Schuchmann & Schubert, 2001; Leong, Wooster, Kentish & Ashokkumar, 2009). Emulsifiers are surface-active molecules that adsorb to the surface of freshly formed droplets during homogenisation. The emulsifiers form a protective membrane that prevent the droplets from coming close enough together to aggregate (McClements, 2005). Emulsions are thermodynamically unstable and can breakdown over time due to physicochemical mechanisms (McClements, 2012). The physical stability of emulsions is discussed in details in section 2.3.1.

The homogenisation process is divided into primary and secondary process (Figure 2.2). The process is dependent on a balance between two opposing physical processes, i.e. droplet disruption and droplet coalescence (McClements, 2005). The initial stages of droplet disruption involve the breakup and intermingling of the bulk oil and aqueous phases to ensure even dispersion of the liquids (primary homogenisation). This is followed by secondary homogenisation, where larger droplets are further disrupted into smaller ones. Droplet coalescence, on the other hand, is when two or more droplets merge to form a single larger droplet. Formation of sufficient concentration of emulsifier membrane around the droplets (during homogenisation), before they have time to collide with each other can help prevent droplet coalescence.



(McClements, 2005)

Figure 2.2. Primary homogenisation of two bulk liquids (oil and water) into an emulsion, and secondary homogenisation, the reduction in the size of the droplets in an existing emulsion

The major components in any emulsion-based system are the droplets, and the physicochemical and functional properties of such systems require control of the particle size distribution as well as the droplet charge and other interfacial properties (McClements, 2012). Smaller oil droplet sizes are reported to improve the optical transparency, increase physical stability, and improve the bioavailability of lipophilic components (McClements & Rao, 2011). Qian, Decker, Xiao and McClements (2011) demonstrated that modified starch could be used to form stable emulsions with small droplet diameters (d < 300 nm) that was stable to several environmental stresses (pH, ionic strength, or temperature). This they attributed to strong steric (rather than electrostatic) stabilisation because polysaccharides form thick hydrophilic polymeric coatings around lipid droplets (Charoen, Jangchud, Jangchud, Harnsilawat, Naivikul & McClements, 2011).

Electrical charges on droplet depending on the nature of the ionized components at their surfaces may range from highly negative to highly positive (McClements, 2012), and this can be controlled by selection of emulsifier type. Droplets can be made to have a negative charge by using anionic surfactants to prepare them (Kralova & Sjöblom, 2009) or a positive charge by using cationic surfactants (Asker, Weiss & McClements, 2009). The different electrical characteristics of biopolymers influence the charge present on droplets (McClements, 2011). Droplets stabilised by commercial polysaccharide emulsifiers such as gum Arabic and modified starch have a net negative charge due to the presence of anionic groups (e.g., sulfate or carboxyl) on the polymer chains (Charoen *et al.*, 2011). On the other hand, droplets stabilised by proteins (e.g., whey protein, casein, soy proteins, egg proteins) have a net charge that depends on the pH of the solutions relative to the isoelectric point (pI) of the adsorbed protein (Schmelz, Lesmes, Weiss & McClements, 2011).

2.1.3 Mayonnaise

2.1.3.1 Definition and characteristics

Mayonnaise is a semi-solid, oil-in-water emulsion and is typically described as a high-fat and high-calorie food (Mun, Kim, Kang, Park, Shim & Kim, 2009; Lee, Lee, Lee & Ko, 2013). The worldwide consumption of mayonnaise and its availability in most homes makes it a very convenient food product. Commercial mayonnaise typically contains egg yolk, salt, vinegar, thickening agents, flavouring materials and oil (Smith & Hui, 2008). Generally, a mayonnaise product is expected to have a “creamy” texture and mouthfeel, a “rich” taste, a characteristic "yellowish-white" appearance, and an extended shelf-life at ambient storage (McClements & Demetriades, 1998). The traditional mayonnaise emulsion contains 70-80 % fat (Depree and Savage, 2001) and "light" mayonnaise products, contain about 36 % fat (McClements, 2005).

The Codex Alimentarius Commission (1989) required that mayonnaise contained at least 78.5 % total fat and 6 % pure egg yolk. The United States law requires that mayonnaise contains not less than 65 % vegetable oil by weight (U. S. Code of Federal Regulations, 2006). In South Africa, mayonnaise, as an emulsion, should contain at least 52 % edible vegetable oil by volume, acidifying agent and either egg or modified milk protein (RSA, 2000). It may, however, contain permitted ingredients such as water, salt, sweeteners, mustard, spices, preservatives, and stabilisers or thickeners either singly or in combination.

2.1.3.2 Ingredient functionality

The interactions between the primary ingredients (oil, vinegar and egg) used in the formulation of mayonnaise emulsions are of interest to food processing and worth studying. Table 2.1 summarizes the different ingredients and their functionalities in the manufacture of mayonnaise. These ingredients play very critical roles by interacting either physically or chemically to provide key quality characteristics to the emulsion. In mayonnaise production, oil forms a greater percentage of the ingredients and hence, the quality of the oil is very critical. It is important that oils used for mayonnaise production do not crystallize (cloud) during refrigeration (e.g., 0°C for 5.5 h), to prevent emulsion instability through partial coalescence (Hui, 1992).

Table 2.1. Ingredients and their functionalities in food emulsions

Ingredients	Type of Ingredient	Role on quality characteristics	References
Oil		- Provide viscosity, texture, stability, lubricity, flavour & appearance	Yang & Lal, 2003, McClemment 1998, Duncan, 2004
Egg	Stabiliser & Emulsifier	- Lower interfacial tension between oil and water - Form protective film around the oil droplets to prevent coalescence	Rousseau, 2000, Ma & Boye 2013
Vinegar	Acidifying ingredients	- Provides flavour - inhibit microbial growth	Duncan, 2004, Depree 2001, Smittle 2000
Salt	Seasoning	- reduce water activity thereby inhibit microbial growth - neutralize the charges on proteins to increase adsorption of egg protein to the oil droplet surface	Duncan, 2004, Depree 2001
Mustard	Seasoning	- Provide flavour - Increase antibacterial activity	Wilson 2013, Jang *et al*., 2010
Fat replacers	Thickeners	- Increase viscosity - provide mouthfeel - contribute to desirable texture - give body to the product	Akoh, 1998, Lucca &Tepper, 1994, McClement 2005

2.2 REDUCED-FAT MAYONNAISE EMULSIONS

2.2.1 Definition and characteristics

Reduced-oil mayonnaise is an oil-in-water emulsion that contains all the permitted ingredients in a full-fat mayonnaise but with edible vegetable oil content between 25 % and 39 % (RSA, 2000). Table 2.2 shows the different fat contents for mayonnaise and salad dressings in South Africa. Alternative terms given to such emulsions include, "reduced fat" (RF), "light," "low fat," or "fat-free" (Mun *et al.*, 2009). The relation between excessive intake of dietary fat and lifestyle changes and the increased prevalence of diet-related non-communicable diseases such as cardiovascular disease and diabetes (Vorster *et al*., 2013), necessitated the production and development of low-calorie, low-fat foods. In such foods, portions of fat are replaced with fat replacers to imitate some functional properties of fat.

In developing low-calorie mayonnaise, non-fat ingredients such as gums, starches, and proteins with different functionalities are incorporated into the formulation as fat replacers. This results in the loss of some quality attribute in low-fat products compared to full-fat products (McClements & Demetriades, 1998). Addition of a new fat replacer should not only improve processing functionalities but must contribute to nutritional benefits. For instance, polysaccharides with high dietary fibre content can lower cholesterol levels (Laneuville, Paquin & Turgeon, 2005).

Table 2.2. Fat Contents of mayonnaise and salad dressings in South Africa

Product	Edible vegetable oil (%)
Mayonnaise	≥ 52
Reduced oil mayonnaise	$25 \leq 39$
Salad cream	≥ 25
Reduced oil salad cream	$13 \leq 18$
Salad dressing	$12 \leq 50$
Reduced oil salad dressing	$0.5 \leq 12$
Oil-free salad dressing	≤ 0.5

Adapted from: (RSA, 2000)

However, due to the multi-functional roles played by fat, the sensory qualities of some foods formulated with fat replacers do not compare favourably to their full-fat counterparts especially in terms of flavour attributes (Akoh, 1998; McClements & Demetriades, 1998). This makes it difficult for people to maintain a reduced-fat dietary regime as consumers want food to taste good. The major challenge facing the food industry is finding 'fat replacers' that can effectively maintain the physicochemical and sensory attributes derived from fat.

2.2.2 Fat-replacers

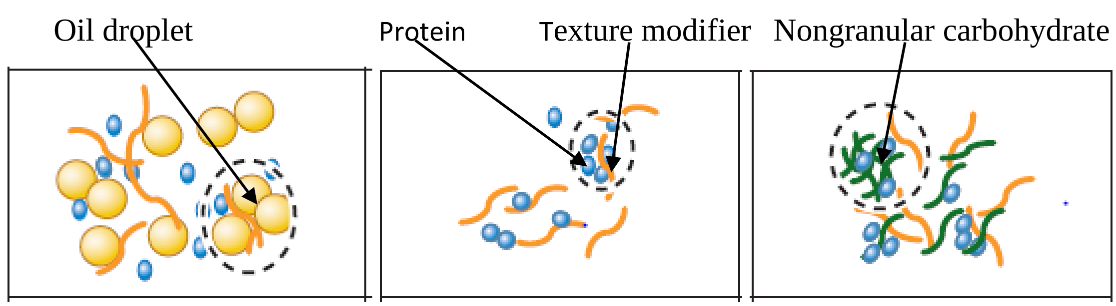
Fat replacers are incorporated into low-fat foods to replace some lost qualities when fat is removed (Ognean *et al*., 2006). Fat replacers may be produced from fat, protein, or carbohydrate and are characterized into two groups - fat substitutes and fat mimetics.

Fat substitutes resemble triglycerides (conventional fats and oils) physically and chemically (Akoh, 1998). They can supposedly replace the fat in foods on a gram-for-gram basis and often referred to as lipid- or fat-based fat replacers. Fat substitutes are chemically synthesized or a derivative of enzymatic modification of conventional fats and oils. Many fat substitutes are stable at cooking and frying temperatures (Akoh, 1998). They are typically synthetic molecules that provide no energy (calories) or structured lipid molecules that provide reduced energy. Common known fat substitutes include Olestra (Olean®), Caprenin and Salatrim.

Fat mimetics, on the other hand, only imitate the sensory or physical properties of triglycerides. They are often protein- or carbohydrate-based, are common food constituents such as starch, pectin and cellulose, but may be chemically or physically modified to mimic the function of fat. Fat mimetics, cannot replace some nonpolar functional characteristics of fats, such as lipid-soluble flavour-carrying capacity, due to their polar nature. The diverse functional properties of fat mimetics, enable them to mimic some of the physicochemical attributes and desirable eating qualities of fat, including, viscosity, mouthfeel and appearance (Ognean *et al*., 2006).

Examples of carbohydrate-based fat mimetics include gums, maltodextrins and dextrins, polydextrose, cellulose derivatives, starch derivatives, and oat flour derivatives (O'Connor & O'Brien, 2011). A well-known commercial protein-based fat mimetic is Simplesse®. Simplesse® is produced by microparticulation of whey protein concentrate ((Akoh, 1998). In general, protein-based fat mimetics are produced through microparticulation of proteins (e.g. egg, milk, whey, soy, or wheat proteins), a process that involves heating the proteins to produce a gel structure (O'Connor & O'Brien, 2011). Very small spherical (0.1–2.0 mm diameter) protein gels are formed during the formulation. This is as a result of high shearing force applied to large gel particles during the process to microparticulate the proteins, causing them to coagulate (heat-coagulated proteins). The particles produced are too small to be perceived as individual rough particles in the mouth. Instead, they are perceived in the mouth and taste buds as similar to fat with a creamy, smooth texture.

Generally, carbohydrate-based fat replacers mimic some textural and functional properties of fat by stabilizing substantial quantities of water in a gel-like matrix (Lucca & Tepper, 1994; Cho & Prosky, 1999). Peng and Yao (2017) further explained the behaviour of fat replacers in a model system such as salad dressing. In a full-fat system, the microstructure consists of fat particles that exist either as individuals or in coagulate units that are close to each other with restricted movements (Figure 2.3). However, in reduced-fat systems, the microstructure is different. The carbohydrate fat replacers may undergo gelation or aggregation, which not only produces microstructured particles in large sizes but also mimics the behaviours of microstructured fat particles during deformation.



Full-fat system | Fat-free system | Fat-free system with carbohydrate fat replacers

(Peng & Yao, 2017)

Figure 2.3. Schematics showing the functionalities of various carbohydrate fat replacers in concentrated liquids (e.g., salad dressing)

2.2.2.3 Fat replacers and the production of low-fat mayonnaise

Several studies have investigated the effect of different fat replacers in the production of reduced-fat mayonnaise emulsions. Lee *et al.* (2013) replaced 30 % of edible oil with gelatinized rice starch and xanthan gum in the formulation of reduced-fat mayonnaise. They produced stable thixotropic emulsions with improved viscosity and decreased calorie value (23 %) compared with full-fat mayonnaise. Chemically modified octenyl-succinic anhydride (OSA) corn and OSA-sorghum starches were successfully used to develop low-fat (75 % fat-replaced) mayonnaise. The low-fat mayonnaise had similar textural characteristics to full-fat mayonnaise and scored higher than full-fat mayonnaise for overall acceptability (Ali, Waqar, Ali, Mehboob & Hasnain, 2015). Ansari, Ali and Hasnain (2017) also chemically (succinylation, hydroxypropylation, and acetylation) modified isolated water-chestnut starches and used it in combination with native starch to prepare low-fat mayonnaise by replacing 80 % of oil. However, concerns about safety related to the use of chemicals have encouraged the development of ‘clean label’ starches (Maphalla & Emmambux, 2016).

Other researches include the application of spent brewer’s yeast β-glucan as a fat replacer in reduced-fat mayonnaise (Worrasinchai *et al*., 2006); the use of 4-α-glucanotransferase-treated rice starch to produce reduce fat mayonnaise (Mun *et al.*, 2009). Teklehaimanot *et al*. (2013) reported the potential of maize and teff starches modified with stearic acid as fat replacers in low-calorie mayonnaise-type emulsions; the use of micro-particulated whey protein (MWP) in combination with either modified starch or locust bean gum (LBG) to fabricate reduced-calorie emulsion-based sauces and dressings (Chung, Degner & McClements, 2014); and more recently, the use of extruded flour-water paste in the formulation of mayonnaise-like emulsions (Román, Martínez & Gómez, 2015).

2.2.3 Starch as fat replacers

2.2.3.1 Starch modification

Native starch, a natural biopolymer, has several limitations in the food industry due to shortcomings in their physical and chemical properties (Singh, Kaur & McCarthy, 2007). They have low thermal and shearing stability and tend to retrograde easily (BeMiller, 2011; Maphalla & Emmambux, 2016), limited solubility in water, they have tendencies to gel and undergo syneresis (Tovar, Melito, Herrera, Rascón & Pérez, 2002). Starches are therefore modified by chemical, enzymatic and physical processes to improve its properties such as thickening, binding, mouthfeel, gelling, and water retention ability (Singh *et al.*, 2007) and also to enhance paste clarity and sheen, paste and gel texture, film formation and adhesion (BeMiller & Whistler, 2009).

In recent times, the demand for 'clean label' modification of starches is high (Chareonthaikij, Uan-On & Prinyawiwatkul, 2016), this is due to concerns about consumer and environmental safety associated to the use of chemicals (Zia-ud-Din *et al*., 2017). Starches and lipids are major food ingredients that have functional interactions in food systems (Tang & Copeland, 2007). Amylose present in starch can form complexes with ligands such as fatty acids and lipids during starch gelatinisation (Putseys *et al*., 2010). Stearic acid and monoglycerides as friendly food chemicals, were used to modify maize and teff starches to obtain 'clean label' starches (D'Silva *et al*., 2016). The modification produced a high viscosity paste and non-gelling starch (D'Silva *et al.*, 2011). The non-gelling was due to an interaction between amylose and stearic acids to form amylose lipid complexes and the latter prevented amylose double helices formation. Thus, amylose molecules are not available to associate with each other to form junction zones and gel network. In a related study, both Type I and Type II amylose-lipid complexes were also formed when maize and teff starches were pasted with stearic acid for short (11.5 min) and prolong (130 min) pasting at 91 °C respectively (Wokadala, Ray and Emmambux, 2012). Also, the formation of type II amylose-lipid complexes was observed when high amylose maize starch was heated with stearic acid at 90 °C for 90 min (Ocloo, Minnaar and Emmambux, 2016).

Teklehaimanot *et al.* (2013) investigated the potential of some of these 'clean label' lipid-modified starches that contain amylose-lipid complexes, as a fat replacer in the formulation of low-calorie emulsions. In the study, it was found that replacing sunflower oil at 50 % and 80 % with the lipid-modified starches produced low-calorie mayonnaise type emulsions with higher viscosity and smaller oil droplets compared to full-fat mayonnaise. All the samples were stable to freeze-thaw cycles and high-temperature during a storage period of 28 days. Low-calorie mayonnaise type emulsions had a 76 % lower calorific value compared to the full-fat mayonnaise. The following section discusses the principle and formulation of amylose-lipid complexes in detailed.

2.2.3.2 Principle and formation of amylose-lipid complex

Three main principles have been documented for the formation of amylose-inclusion complexes. The first involves starting the modification process with starch and the ligands. The second involves working directly with amylose and the ligands, and the third involves, synthesizing the amylose in the presence of the ligands (Putseys *et al.*, 2010). Each category gives rise to different amylose-inclusion characteristics with complexes obtained from the last two methods being purer and mono-dispersed (Putseys *et al.*, 2010). Obiro, Sinha Ray and Emmambux (2012) classified the production of ALCs roughly into three methods; classical, enzymatic, and thermo-mechanical processing methods. The classical method involves mixing amylose-containing starch fraction and a ligand under shear-less heating/moisture conditions. In the case of the enzymatic method, ALCs are formed either utilizing a bottom-up approach catalyzing preparation from glucosyl residues or a top-bottom approach which involves a combination of enzymatic starch hydrolysis and the use of the classical procedure (Obiro *et al.*, 2012). The third option, the thermo-mechanical method, utilizes thermal processing technologies to produce ALCs through "green" chemistry methods than the previous two (Panyoo & Emmambux, 2017). This method involves the simultaneous use of heating and shearing effects to produce ALCs. Different thermal processing technologies have been reviewed by Panyoo and Emmambux (2017) and summarized in Table 2.3.

Table 2.3. Production of amylose–lipid complex at different thermal processing condition

Method	Condition	Sample	Type of lipid	Type of amylose-lipid complex	References
Steam jet cooking	Heating at 140°C and cooled rapidly or slowly	High amylose corn starch (70%)	Palmitic acid	No type of complex have been characterized	Fanta, *et al*., 2008
Heat high pressure homogenisation	Heating with high pressure of 100 MPa	Defatted corn starch	Lauric acid	Type II	Meng, et. al., 2014
Extrusion cooking	Tb: 128°C Screw speed:140 r.m.p	Rice starch	Oleic acid	Type I	De Pilli, et. al., 2011,
	Tb: 160°C, Screw speed: 160 rpm	Maize starch	Inherent lipids		Genkina, 2015
Wet heating process	Long pasting time (130 min)	Tef and maize starch	Stearic acid	Type II	Wokadala *et al*, 2012, D'Silva, *et. al*., 2011
	Short pasting time (11.5 min)	Tef and maize starch	Stearic acid	Type I	Wokadala *et al*, 2012, D'Silva, *et. al*., 2011
Enzymatic debranching & Heating process	Addition of *Bacillus acidopullulytics* pullulanase (40 U/g starch) & Heating at 90 °C	High amylose corn starch (70%)	Stearic acid	Type I & Type II	Reddy *et al*, 2018

Single amylose chains form complexes with a range of complexing agents. These include fatty acids, emulsifiers, and smaller ligands, such as alcohols or flavour (Le Bail, Rondeau & Buleon, 2005). These complexing agents induce the formation of a compact helical conformation of amylose, displaying the V-type diffraction pattern (Putseys *et al*., 2010). Single helix amylose (V-amylose) has a hydrophilic glycosyl hydroxyl exterior surface with a distinctly hydrophobic inner channel lined with methylene groups and glycosidic linkages (Obiro *et al*., 2012). Lipids form complexes with amylose when the hydrophobic aliphatic fatty acid chain of the lipids goes to reside in the hydrophobic core within the V-amylose helix through hydrophobic forces (Figure 2. 4) (López *et al*., 2012; Obiro *et al*., 2012; Chao, Yu, Wang, Copeland & Wang, 2018). Inside the cavity, the amylose-lipid interactions are stabilised by molecular hydrogen bonds and van der Waals forces between the amylose glucose residues, water molecules and the lipid (Nimz, Gessler, Usón, Sheldrick & Saenger, 2004).

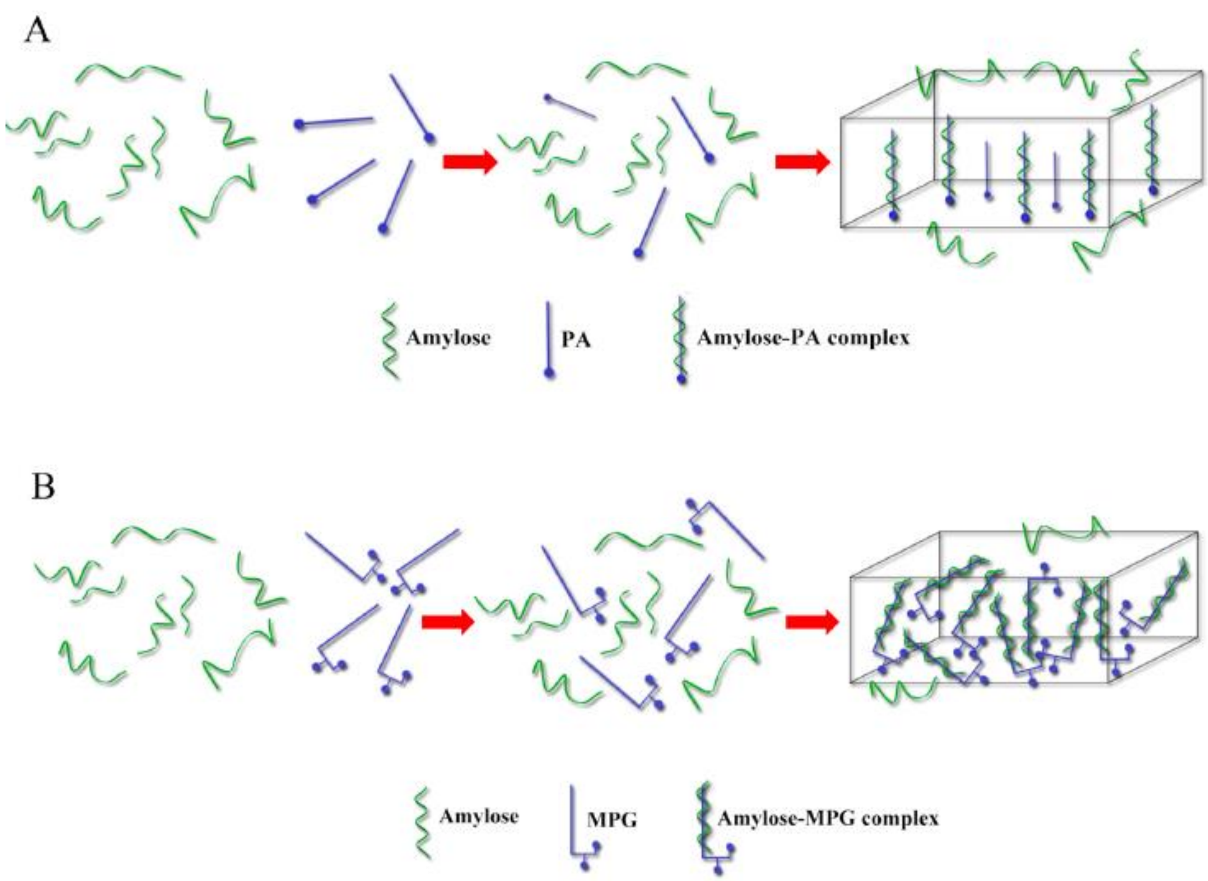


Figure 2.4. Mechanisms showing the formation of starch−lipid complexes (A) amylose-palmitic acid (PA) (B) amylose-monopalmitate glycerol (MPG)

(Chao *et al*., 2018)

Two kinds of V-amylose complexes have been reported. Type I, formed at low temperature (≤ 60 °C) where the amylose-inclusion complexes consist of a partially ordered structure with no distinct crystalline regions. And Type II formed at a higher temperature (≥ 90 °C) and has more organized lamellae with distinct crystalline and amorphous regions (Putseys *et al.*, 2010). Biais, Le Bail, Robert, Pontoire and Buleon (2006) demonstrated the possible morphology of the V-amylose complexes as a lamellar with alternating crystalline and amorphous layers. They reported the ligand to be positioned in three possible locations; within the helices, between the helices of the crystalline regions or dispersed in the amorphous regions Figure 2.5.

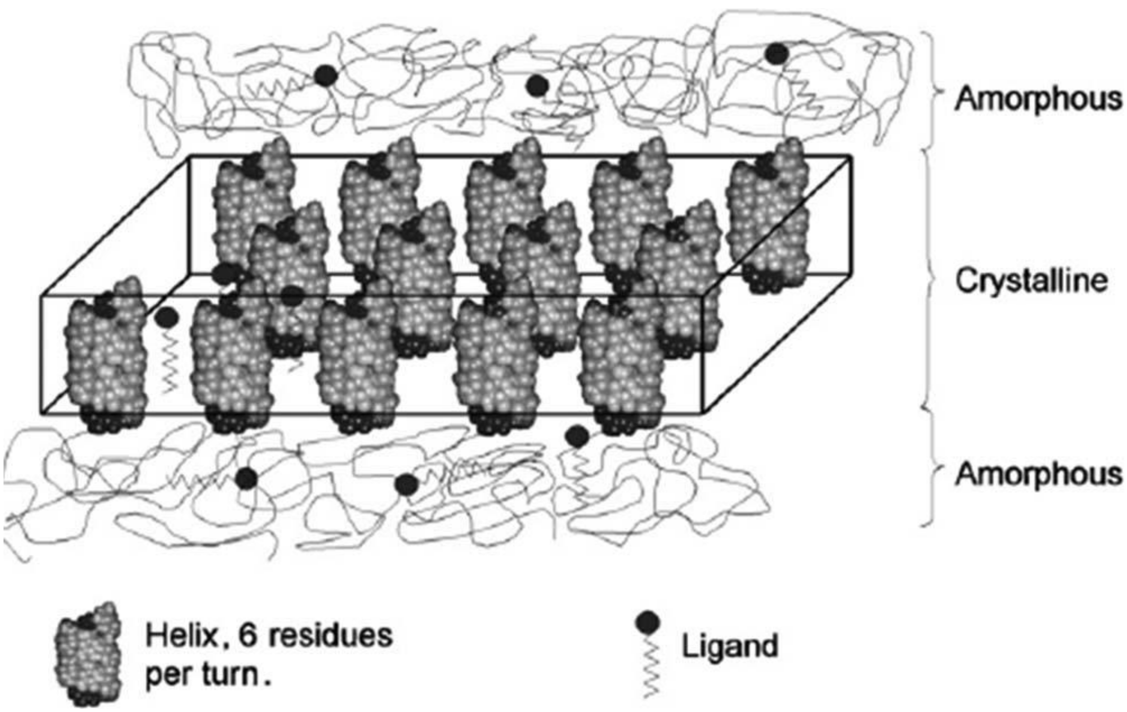


Figure 2.5. Schematic representation of the lamellae-like structure of amylose-ligand complexes and possible ligand of molecules trapped

(Biais *et al.*, 2006)

A number of factors affect the formation of the V-amylose complexes, which Obiro *et al.* (2012), divided into two; reactant factors (starch type, water content of the starch, starch degree of polymerisation, starch/ligand concentration ratio, and the structure of the included molecule) and the experimental factors (complexation temperature, complexation time, and the pH of the medium). Derycke, Vandeputte, Vermeylen, De Man, Goderis, Koch and Delcour (2005), concluded that the variety of rice, the moisture content and moisture distribution in the rice kernel impacted on the formation and crystallization of V-amylose complexes. The effect of temperature on complexation was demonstrated by Gelders, Vanderstukken, Goesaert and Delcour (2004) when more of type I complexes were formed at 60 °C and more type II complexes formed at 90 °C. Longer heat treatment (> 2 hrs) favour formation of complex type II V-amylose relative to the formation of Type I (Tufvesson, Wahlgren & Eliasson, 2003a, b; Wokadala, Ray & Emmambux, 2012). Long chain fatty acids (between 14, 16 and 18 carbon chain) and lower degree of unsaturation form more thermally stable complexes (Gelders *et al*., 2004; Putseys *et al.*, 2010). Tang and Copeland (2007) established that maximal complex formation is related to the water solubility and critical micellar concentration of the lipid and occurs at a different concentration for different lipids. In a starch-lipid-water system, the lipid molecules can either interact with the solvent water to form complexes with amylose, or self-associate into micellar structures. For fatty acids, the critical micelle concentration (the concentration at which micellar aggregation first occurs) decreases as carbon chain length increases and water solubility decrease.

2.2.3.3 Functionality and importance of amylose-lipid complexes

Amylose-lipid complexes (ALCs) have several functionalities and importance in the food industry. The tendency of native starches to retrograde was reduced by the formation of amylose-lipid complexes (Arocas, Sanz & Fiszman, 2009). In a study to determine the effect of stearic acid on the functionality of teff and maize, the resultant paste had a softer texture and reduced retrogradation tendencies during cooling and storage (Maphalla & Emmambux, 2016). During pasting of cereals in the presence of lipids, the formation of amylose-lipid complexes was reported to increase paste viscosity (D'Silva *et al.*, 2011), and resulted in the formation of a second viscosity peak (Nelles, Dewar, Bason & Taylor, 2000; Wokadala *et al.*, 2012). Teklehaimanot *et al*. (2013), reported the potential of amylose-lipid complexes formed after modification of maize starch with stearic acid as fat replacers in food emulsions.

Different flavour compounds form helical inclusion with amylose (Wulff, Avgenaki & Guzmann, 2005). Therefore encapsulation into amylose complexes can be used to stabilise volatile flavour compounds, thereby increasing their retention (Arvisenet, Voilley & Cayot, 2002). Amylose-flavour complexes influence flavour release in starch-based foods and can be used in food where a controlled flavour release is desired (Heinemann, Zinsli, Renggli, Escher & Conde-Petit, 2005).

Amylose-lipid complexes have several health benefits. In a review by Panyoo and Emmambux (2017), they reiterated the potential health benefits of ALCs, as resistant starch and having the health benefits of dietary fibre. Wang, Wang, Yu and Wang (2016), in their study, reported that complexes formed between starch and fatty acids were more resistant to amylase digestion compared to starch without fatty acid. Another health benefit associated with ALCs is that the formation of V-amylose complexes reduce the digestibility of starch and thus control glycemic response (Gelders, Duyck, Goesaert & Delcour, 2005). Also, amylose-conjugated linoleic acid complexes are reported to provide stability to oxidation and thermal treatments and can serve as a vehicle for delivery of polyunsaturated fatty acids (PUFA) to the intestine (Lalush, Bar, Zakaria, Eichler & Shimoni, 2005).

2.3 QUALITY CHARACTERISTICS OF EMULSIONS

2.3.1 Physical stability

The physical stability of an emulsion is governed by changes in the spatial distribution of its various ingredients (McClements & Demetriades, 1998). Emulsions are thermodynamically unstable systems due to the high interfacial tension between oil and water molecules. Differences in densities of the oil and water phases tend to cause an emulsion breakdown over time. Preparation of emulsions that are kinetically stable over some time requires the incorporation of emulsifiers and thickening agents (McClements & Demetriades, 1998).

Several physicochemical mechanisms are responsible for the physical breakdown of food emulsions. The most important being creaming/sedimentation, flocculation, coalescence, partial coalescence, phase inversion and Ostwald ripening (Figure 2.6). Creaming being the process in which droplets, due to gravity, move upward because of their lower density compared to the continuous phase. In the situation where the droplets have a higher density, the droplets move downwards due to gravity and this process is known as sedimentation. The rate of gravitational separation can be retarded by decreasing particle sizes or by adding thickening or gelling agents to increase the viscosity of the aqueous phase (Degner, Chung, Schlegel, Hutkins & McClements, 2014).

In an emulsion, droplets either exist as individual entities, or aggregate with each other through the process of flocculation, coalescence, or partial coalescence (McClements, 2005). Flocculation is the process in which two or more droplets 'stick' together to form an aggregate in which the droplets retain their individual integrity. Droplet flocculation can affect the stability and rheology of food emulsions (Degner *et al.*, 2014). This is because, in dilute systems, droplet flocculation can lead to increased creaming due to an increase in particle size; thus, reducing the stability of the emulsion. On the other hand, in relatively concentrated emulsions, the aggregated droplets can inhibit creaming by forming a 3-dimensional network causing an appreciable increase in the viscosity or gel strength of the emulsion. Coalescence is the process in which two or more droplets merge to form a single larger droplet. The rate of occurrence of coalescence depends strongly on the nature of the layer of surface-active molecules that coats the fat droplets (Degner *et al.*, 2014). An interfacial layer around the fat droplets capable of generating a strong repulsive force and has mechanical properties that resist disruption can be relatively stable to coalescence. Flow-induced coalescence was reduced after the addition of some proteins and polysaccharides that were able to form interfacial layers that are highly resistant to coalescence in highly-concentrated protein-stabilised emulsions (van Aken, 2003; van Aken, Blijdenstein & Hotrum, 2003). Partial coalescence involves the merger of two or more partly crystalline droplets to form a single irregularly shaped aggregate. This phenomenon occurs when a solid fat crystal from one droplet penetrates into a region of liquid oil in another droplet. Partial coalescence may lead to an increase in product viscosity and the presence of visible lumps in an emulsion (Degner *et al.*, 2014).

The process of phase inversion involves a change between emulsions i.e.an oil-in-water emulsion changes to a water-in-oil. In the case of Ostwald ripening, varying droplet sizes within an emulsion favours the growth of larger droplets at the expense of smaller droplets due to molecular diffusion of oil molecules through the aqueous phase separating the droplets (McClements, 2005). The solubility of the substance within the droplet in the continuous phase surrounding the droplet, increases with decreasing droplet radius. In other words, there is a higher concentration of solute around a small droplet than around a larger droplet (Julian

McClements, Henson, Popplewell, Decker & Jun Choi, 2012). Solute molecules then move from the smaller droplets to the larger droplets because of the difference in a concentration gradient.

Factors influencing the stability of an emulsion include particle size, emulsifier type, and pH and ionic strength of the aqueous phase of an emulsion. The rate of gravitational separation, droplet flocculation or coalescence decreases as the droplets size decreases (McClements, 2005). Therefore, the stable emulsion can be obtained by reducing the initial particle size during homogenisation, and ensuring that droplet aggregation does not occur afterwards. The nature of emulsifier used affect the size of droplets generated during homogenisation. This eventually influences the stability of the emulsion to gravitational separation and aggregation. The nature of the adsorbed emulsifiers after emulsion formation, also, determines the stability of the emulsion to environmental stresses such as; pH, ionic strength, and temperature changes. Protein-coated fat droplets are highly sensitive to pH and ionic strength because they are mainly stabilised by electrostatic repulsion (McClements, 2004), while nonionic surfactant-coated and polysaccharide-coated fat droplets are less sensitive to pH and ionic strength because they are mainly stabilised by steric repulsion (Qian *et al.*, 2011). The pH and salt concentration of the aqueous phase affect the stability of the emulsion due to the effect they have on the electrostatic interactions in the system (McClements, 2004; McClements, 2005).

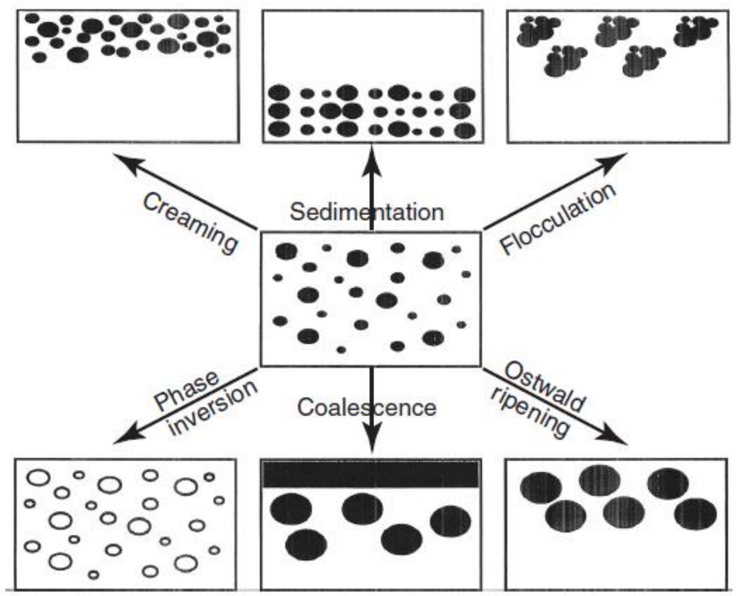


Figure 2.6. Schematic diagram of the various breakdown processes that occur in food emulsions: flocculation, coalescence, creaming, sedimentation, Ostwald ripening and phase inversion

(Tadros, 2013)

2.3.2 Chemical stability

Lipid oxidation describes a series of chemical changes that involve the interaction of lipids with oxygen-active species (McClements & Decker, 2000). The process causes deterioration of unsaturated lipids leading to an undesirable chemical change that may impact flavour, texture, nutritional quality and produce toxic compounds (McClements & Decker, 2000; Waraho, McClements & Decker, 2011). The processes of auto-oxidation occur via a complex, radical chain reaction generally divided into three phases: an initiation phase, a propagation phase, and a termination phase (McClements & Decker, 2000; Gorji, Smyth, Sharma & Fitzgerald, 2016). During the initiation phase, external energy, such as light, acts on unsaturated lipid molecules or fatty acids, in the presence of catalysts e.g. transition metal, to generate a free radical by losing a hydrogen atom. This is followed by the propagation phase, where molecular oxygen combines with unsaturated fatty acids to produce hydroperoxides and free radicals, both of which are very reactive. These reactive products, in turn, react with additional lipid molecules to form more reactive chemical species. At this stage, lipid peroxyl radicals (ROO^*) and hydroperoxides (ROOH) are the primary oxidation products. These primary products decompose into secondary oxidation products (hydrocarbons, alcohols, aldehydes, ketones, volatile organic acids and epoxy compounds) which are responsible for the off-flavour and off-odour in oil (Gorji *et al.*, 2016). In the final, termination phase, relatively unreactive compounds are formed such as oxidized polar/non-polar dimers or trimers of lipids.

The mechanism of lipid oxidation in oil-in-water emulsions is more complex and differs from that for bulk lipid systems (Waraho *et al*., 2011; Gorji *et al.*, 2016). The rate of oxidation is influenced by the emulsion composition and the partition of the emulsifier between the interface and the water phase (Kiokias *et al*., 2009). This is due to the presence of the aqueous phase, which contains both pro-oxidants and antioxidants and an oil-water interface that impact interactions between oil and water components (McClements & Decker, 2000). In complex food systems such as mayonnaise, several factors affect the process of oxidation. These include; temperature, light, chemical structure of lipids, oil concentration and emulsifier type (Lennersten & Lingnert, 2000; Depree & Savage, 2001; Nuchi, McClements & Decker, 2001; Lagunes-Galvez, Cuvelier, Ordonnaud & Berset, 2002; Sørensen, Nielsen, Hyldig & Jacobsen, 2010a; Sørensen, Nielsen & Jacobsen, 2010b; Li, Kim, Li, Lee & Rhee, 2014).

Generally, the susceptibility of monounsaturated fatty acids such as oleic acid to oxidation is lower than that of PUFAs, and the rates of lipid oxidation increase with lipid unsaturation (Berton-Carabin, Ropers & Genot, 2014). This is because, in the presence of a double bond in a fatty acid chain, the dissociation energy of the C-H bonds located on the allylic carbons is weakened (from around 100 to 74 kcal/mol), making the removal of the hydrogen easier, and for a bis-allylic C-H bond, the dissociation energy is substantially lower (65 kcal/mol) (Schaich and others 2013). For instance, the formation of conjugated diene hydroperoxides increased with the linoleic acid content of the oil in emulsions prepared with different dietary oils (Kiokias, Dimakou, Tsaprouni & Oreopoulou, 2006).

The type of emulsifier used impacts on the formation of a biopolymer layer at the emulsion droplet interface and affects the rate of lipid oxidation (Djordjevic, Cercaci, Alamed, McClements & Decker, 2007; Shaw, McClements & Decker, 2007; Sørensen *et al.*, 2010a). Large molecular-sized emulsifiers have been reported to form a barrier that decreases interactions between lipids and aqueous phase pro-oxidants thus retarding the rate of lipid oxidation (Silvestre, Chaiyasit, Brannan, McClements & Decker, 2000; Kiokias *et al*., 2006;

Waraho *et al.*, 2011). This is in agreement with earlier research by Fomuso, Corredig and Akoh (2002), where a higher concentration of emulsifier (1%) resulted in lower oxidation rates compared to 0.25% emulsifier in model oil-in-water emulsions prepared with saturated lipids.

Polysaccharides used as fat replacers, stabilisers and thickeners in oil-in-water emulsions have been reported to have the ability to inhibit lipid oxidation mainly attributed to their free radical scavenging, transition metal binding, and viscosity enhancement properties (Waraho *et al.*, 2011). Transition metals, eg. iron, close to lipid hydroperoxides at the lipid droplet interface promote hydroperoxide degradation (Charoen, Jangchud, Jangchud, Harnsilawat, Decker & McClements, 2012). Hu, McClements and Decker (2003) proposed that negatively charged lipid droplets attract positively charged transition metals to their surfaces, thereby bringing the pro-oxidant into proximity to the lipid substrate and increasing the rate of oxidation. Rice bran oil emulsions containing modified starches and whey protein isolate coated lipid droplets were relatively stable to lipid oxidation, compared to negatively charged gum arabic coated droplets that were highly unstable to oxidation (Charoen *et al.*, 2012). Several types of research have proposed that other physicochemical properties of biopolymers can affect the rate of lipid oxidation. A thick densely packed interfacial coatings formed by a biopolymer would effectively prevent the diffusion of transition metals from reacting with emulsified lipids (Paraskevopoulou, Boskou & Paraskevopoulou, 2007; Charoen *et al.*, 2012). The addition of low-methoxyl and high-methoxyl pectin (0.02-0.1 wt %) reduced the formation of lipid hydroperoxides with an inhibition that increased with increasing polysaccharide concentration in the continuous phase, due to their ability to chelate transition metal ions at negatively charged sites (Chen, McClements & Decker, 2010). Soluble soybean polysaccharides showed a significant radical scavenging activity attributed to the presence of the galacturonic acids that can efficiently entrap radicals (Matsumura, Egami, Satake, Maeda, Takahashi, Nakamura & Mori, 2003). McClements and Decker (2000) reported the antioxidant activity of some polysaccharides, e.g., tragacanth due to their ability to donate hydrogen and therefore act as radical chain breakers, (McClements & Decker, 2000).

High temperature increases the rate of lipid oxidation (Lu, Bruheim, Haugsgjerd & Jacobsen, 2014). Several researchers have confirmed this in their various studies. Lipid oxidation in fish oil-enriched light mayonnaise increased with storage temperature (Sørensen *et al.*, 2010a). Li *et al.* (2014), in their study, found that total oxidation and peroxide values were higher in mayonnaises stored at 25 °C compared with samples stored at 4 °C. In a study to investigate the oxidation stability of cholesterol in mayonnaise during storage, although the oxidation rate generally increased during storage, the total cholesterol oxides formed at 25 °C (30.2 mg/g) were higher than at 4 °C (20.3 mg/g) (Morales-Aizpurúa & Tenuta-Filho, 2005).

Lipids present in foods can undergo oxidative deterioration when exposed to both ultraviolet radiation and visible light (Lennersten & Lingnert, 2000). The deteriorative effect of light can be influenced by the following factors; the intensity and spectrum of the light source, duration of light exposure, food product composition and the light transmittance of the packaging material. Lipid oxidation due to light exposure can be due to either photolytic autoxidation or photosensitized oxidation (Lennersten & Lingnert, 2000; Gorji *et al.*, 2016). Photolytic auto-oxidation occurs when lipids are exposed to ultraviolet radiation, resulting in the production of free radicals (Bradley & Min, 1992). Generally, unsaturated fatty acids do not absorb visible light, but in the presence of photosensitizers and visible light, they undergo photosensitized oxidation (Lennersten & Lingnert, 2000; Gorji *et al.*, 2016). Sensitizer compounds (e.g. natural pigments such as riboflavin and chlorophylls) present in the food are converted to an excited state when light energy is absorbed. These excited compounds interact with the lipid during the formation of free radicals, leading to the formation of highly reactive singlet oxygen (Lennersten & Lingnert, 2000). In a research by Lennersten & Lingnert (2000) to determine the influence of wavelength on lipid oxidation in low-fat mayonnaise, they observed that lipid oxidation was accelerated most by ultraviolet radiation of wavelengths 365 nm, followed by 405 nm and 435 nm. No effect on the lipid oxidation rate was observed when the mayonnaise was exposed to light with wavelengths longer than 470 nm. They attributed the accelerated rate of lipid oxidation at 365 nm to photosensitized oxidation, due to no absorbance of fatty acids in the ultraviolet region. Mayonnaise must, therefore, be protected against wavelengths shorter than 470 nm to prevent the occurrence of light-induced lipid oxidation.

2.3.3 Microbial Stability

Commercial mayonnaise and salad dressing have a shelf-life determined more by their physicochemical characteristics of between 9 - 12 months (Sikora, Badrie, Deisingh & Kowalski, 2008). Commercially produced mayonnaise is rarely implicated in foodborne outbreaks (Smittle, 2000; Duncan, 2004). Acidity and water activity are an essential intrinsic characteristic of mayonnaise that act a precursor for the survival of pathogenic bacteria. These parameters are therefore used in evaluating the quality and safety of salad dressing and mayonnaise products. The highest manufacturing target of pH for dressings and sauces is 4.4, which is reported to be below the inhibitory pH of 4.5 for foodborne pathogens in the presence of acetic acid (Smittle, 2000; Sikora *et al.*, 2008). Acetic acid, the predominant acid in vinegar, gives the mayonnaise a pH range of 3.6 to 4.0 (Smittle, 2000; Duncan, 2004). The aqueous phase contains dissolved sugar and salt, contributing to relatively low water activity (a_w) of 0.929 (Duncan, 2004). However, in reduced-fat, low-calorie products, there is an increase in moisture content due to the increase in the aqueous phase and the high moisture content of fat replacers added. The high moisture content and the reduction of acetic acid in the aqueous phase increases the microbial risk of reduced-fat products. A water activity range of 0.85 to 0.93 and a pH range of 3.3 to 4.1 can inhibit the growth of both yeast and lactobacillus organisms in food products (Martin *et al*. 2000).

Smittle (2000), in a review, reported that several foodborne pathogens (E. coli O157:H7, L. monocytogenes, Salmonella spp., Salmonella Enteritidis, S. aureus, and Y. enterocolitica) died off when inoculated into a variety of mayonnaises, dressings, and sauces. E. coli O157:H7 inoculated at a population of 6.23 log10 CFU/g was not detected in reduced calorie-mayonnaise dressing (pH 4.04 to 4.08) held at 5 °C after 58 days and approached undetectable levels in real mayonnaise after 93 days (Hathcox, Beuchat & Doyle, 1995). Similarly, there was a reduction in the initial population (5.3 log10 CFU/g) of *E. coli* O157:H7 present in coleslaw by 0.1 to 0.5 log10 CFU/g after storage at 21 C for 3 days (Wu, Beuchat, Doyle, Garrett, Wells & Swaminathan, 2002). Growth of *L. monocytogenes* decreased with increase in the pH of seafood salad with mayonnaise (Hwang & Tamplin, 2005). Although numerous researchers have reported on the safety of mayonnaise and salad dressings due to the lack of survival of foodborne pathogens, good manufacturing practices must strictly be adhered to during selection of ingredients and processing.

2.3.4 Effect of fat reduction on the quality characteristics (sensory, tribology and rheology) of reduced-fat mayonnaise emulsions

Several researchers have reported that some characteristics of reduced-fat mayonnaise emulsions do not compare favourably with their full-fat counterparts (McClements, 2002; Worrasinchai *et* *al*., 2006; Lee *et al.*, 2013). For instance, the addition of β-glucan adversely affected the appearance and colour of reduced-fat mayonnaise resulting in significantly lower acceptability as compared with the full-fat control sample (Worrasinchai *et al.*, 2006). Low-fat mayonnaise formulated with different fat mimetics (Liu, Xu & Guo, 2007) and with 50 % potato powder mash (El-Bostany, Ahmed & Amany, 2011), had higher water content than their full-fat and commercial low-fat counterparts. In investigating the influence of locust bean gum (LBG) on the physicochemical properties of model food sauces containing fat droplets, (Chung, Degner & McClements, 2013a) reported a decrease in lightness and flocculation stability of emulsions. Nonetheless, researchers continue to work in earnest toward maintaining and not compromising the quality characteristics of reduced-fat mayonnaise. Knowledge on the tribology (i.e. thin layer lubrication) and bulk rheology of reduced-fat mayonnaise and how it affects the sensory profile of the emulsions can therefore not be overemphasized.

2.3.4.1 Sensory and oral tribology characteristics

Optical properties and appearance

The overall appearance of a food emulsion is greatly dependent on the characteristics (surface gloss, opacity, colour, and homogeneity) of the emulsion (McClements, 2005). Chantrapornchai, Clydesdale and McClements (2000) attributed these characteristics mainly to the interactions that occur between light waves and the emulsion. The opacity and colour of emulsions, are determined by particle concentration, size, refractive index contrast, and the presence of any chromophores that absorb light (Chung *et al.*, 2014). A light that is incident on an emulsion may be reflected, transmitted, scattered, absorbed, and refracted before being detected by the human eye (McClements, 2002).

Increased light scattering ability of fat droplets, increases perceived lightness of an emulsion (McClements, 2002; Chung & McClements, 2014). In reduced-fat products, particle size distribution can be optimised to increase the light scattering efficiency of the oil droplets after reducing the fat droplet concentration (Chung *et al.*, 2014). The target is to fabricate droplets with sizes similar to the wavelength of light (500 nm). Also, by incorporating non-fat particles that effectively scatter light similar to oil droplets can increase the opacity of emulsions (Chantrapornchai *et al.*, 2000).

Flavour profile

The overall flavour profile of a food emulsion is dependent on the distribution of flavour molecules within the oil phase, aqueous phase, interface, and headspace and their release during consumption (Chung & McClements, 2014). The flavour profile of emulsion-based foods depends on the properties (the type of oil, concentration, size, and physical state) of the oil droplets. The concentration of nonpolar flavours in the headspace above an emulsion is reduced, as fat content increases, thus decreasing the perceived flavour intensity of nonpolar flavours (Christiansen, Korhonen, Juszczak, Giebels & Pihlatie, 2011; Mao, Roos & Miao, 2013). In the case of polar flavours, an opposite situation is true (Mao *et al.*, 2013). In full-fat products, flavour intensity is characterized as balanced and sustainable throughout the course of consumption (‘‘sustained release’’), whereas in reduced-fat products the flavour intensity is said to be unbalanced due to an initial spike (‘‘burst release’’) of flavour immediately after consumption, followed by low flavour intensity at later times (Malone & Appelqvist, 2003; Ma & Boye, 2013). Malone and Appelqvist (2003) attributed the initial flavour burst in reduced-fat products, to the increased presences of the non-polar flavour molecules in the aqueous phase than in the oil phase.

One of the major difficulty with developing fat-reduced versions of traditional dressings is the change in the flavour profile as a result of the removal of the fat droplets (Ford, 2004). When the fat content is reduced, the partitioning and release rate of flavour compounds is changed, which changes the flavour profile. The sustained release may be achieved by encapsulating non-polar flavour molecules in delivery systems, such as filled hydrogel particles or microencapsulated particles (McClements, 2015). The presence of non-fat particles and other components such as thickening agents, within the aqueous phase, can influence the perceived flavour characteristics of emulsion-based products by altering the partitioning and mass transport of volatile and non-volatile molecules (Chung *et al.*, 2014). Flavour molecules, depending on their hydrophilic or hydrophobic nature may bind to some proteins and polysaccharides, and cause a change in the flavour profile of the product (Guichard, 2002). The concentration of carbohydrates such as starches and polysaccharides used as thickeners in reduced-fat emulsions, affect the viscosity as well as the rate of flavour retention and release (Naknean & Meenune, 2010). This is due to binding interactions between the flavour molecules and the thickener and reduction in the rate of diffusion as the viscosity increases.

Chung *et al.* (2014) demonstrated the effectiveness of using microparticulated whey protein in combination with either modified starch or locust bean gum to formulate reduced-calorie food emulsions with appearance and consistency similar to those of full-fat emulsions. Puligundla, Cho and Lee (2015), also conducted a study on the characteristics of reduced-fat mayonnaise that they formulated by partial substituting oil with native and chemically (hydroxypropylated and cross-linked hydroxypropylated) modified rice starches in the range 10-50%. Desirable sensory characteristics were obtained for mayonnaise with up to 20 % total oil substitution.

In-mouth texture

Szczesniak (2002) defined texture as 'the sensory and functional manifestation of the structural, mechanical and surface properties of foods detected through senses of vision, hearing, touch and kinesthetic' while mouthfeel is defined as the sensations arising from the interactions of an ingested food (mixed with saliva) with the receptors in the mouth that respond to tactile stimuli during mastication (Smith & Margolskee, 2001). For emulsion-based foods, the type and concentration of fat droplets influence the perceived texture and mouthfeel (Chung & McClements, 2014). In research by Chojnicka-Paszun, De Jongh and De Kruif (2012), a significant correlation was found between creamy attribute and friction coefficient above a fat content threshold concentration of 1 % in milk. Increasing the fat droplet concentration in different sauces increased the consistency of the sauces, and this was highly correlated to mouthfeel viscosity (thickness) derived from sensory analysis (Chung, Olson, Degner & McClements, 2013b). Therefore, the texture and mouthfeel of reduced-fat emulsions are greatly compromised when the concentration of fat droplets is reduced, especially without the incorporation of fat replacers. The sensory ratings for mouthfeel viscosity and yield stress of the model sauce (5% fat) containing locust bean gum were higher than the sauces without locust bean gum (Chung *et al.*, 2013b).

Lubrication behaviour between oral surfaces and food during oral processing is a very important mechanism that relates to food texture and mouthfeel. In emulsion such as mayonnaise, the high oil content coats the oral mucosa during consumption to form a thin film (Malone, Appelqvist & Norton, 2003) and coalescence upon increased shearing during oral processing (McClements, 2005; Dresselhuis, De Hoog, Stuart & Van Aken, 2008). The occurrence of coalescence in the mouth depends on the characteristics of the emulsion, i.e. droplet size, interfacial layer, type of emulsifier and type of fat (Dresselhuis *et al.*, 2008). De Wijk and Prinz (2005) found that measured friction increased with increasing fat droplets size in mayonnaise, and this is a phenomenon associated with high roughness and low creaminess. In reduced-fat mayonnaise, the addition of modified starches such as amylose-lipid complexes reduces the droplet size of the droplets available in the mayonnaise samples (Teklehaimanot *et al.*, 2013). These nano-sized particles of amylose lipid complexes (Zabar, Lesmes, Katz, Shimoni & Bianco-Peled, 2009; Cuthbert *et al*., 2017) used as fat replacers can effectively lubricate the oral cavity by mimicking fat-like properties and thus reduce friction (Chen & Liu, 2006; Wu, Tsui & Liu, 2007; Padgurskas, Rukuiza, Prosyčevas & Kreivaitis, 2013).

2.3.4.1 Rheological characteristics

Mayonnaise and salad dressings are examples of products which show viscoelastic rheological behaviour and also possess yield stress (Ford, 2004). The viscosity of an emulsion is directly related to the viscosity of the continuous phase. Therefore, the addition of components within the aqueous phase for viscosity enhancement, impact on the overall rheology and textural properties of the system (Rao, 2007; Protonotariou, Karali, Evageliou, Yanniotis & Mandala, 2013). Several researchers have reported the influence of the addition of biopolymers, as fat replacers, thickeners or gelling agents on the texture and mouthfeel characteristics of reduced-fat emulsion (Mun *et al*., 2009; Meyer, Bayarri, Tárrega & Costell, 2011; Chung *et al.*, 2013a). These biopolymers stabilize substantial quantities of water in a gel-like matrix, making it achieve functional properties similar to those of fats (Lucca & Tepper, 1994).

Lee *et al.* (2013), successfully formulated reduced-fat mayonnaise by replacing part of the oil with gelatinized rice starch and xanthan gum. Reduced-fat mayonnaise had 23 % lower energy calorie) content and exhibited similar rheological properties (flow and viscoelastic properties) as commercial reduced-fat mayonnaise. In another research, Teklehaimanot *et al.* (2013) explored the effects of teff and maize starches modified with 1.5 % stearic acid on the rheological properties, microstructure, freeze-thaw, and high-temperature stability of mayonnaise-type-emulsions. It was found that replacing sunflower oil at 50 % and 80 % with stearic acid modified maize starch produced low-calorie mayonnaise type emulsions with higher viscosity and smaller oil droplets compared to full-fat mayonnaise.

2.4 CONCLUDING REMARKS

- Reducing the consumption of total dietary fat is a feasible way to help reduce the incidence of obesity in the society, and this is the primary dietary goal for health-conscious consumers. Fat replacers are compounds incorporated into reduced-fat foods to provide them with some qualities of fat. Therefore, foods formulated with fat replacers might be the best choice.
- Several methods have been employed in the production of amylose-lipid complexes, but the thermal processing method uses green chemistry and is best for producing 'clean label' fat replacers to address consumer concerns on safety.
- Researchers have focused mainly on the rheological properties of oil-in-water emulsions that employed the use of amylose-lipid complexes as a fat replacer, with limited research on the lubricating and sensory properties of such emulsions. Hence the need for more research in these areas, especially in complex food systems such as mayonnaise.
- Mayonnaise is a complex high-fat oil-in-water emulsion and therefore understanding the rheological, tribological and sensory characteristics and how they relate to each other is very critical to designing and fabricating a reduced-fat version.

2.5 HYPOTHESES AND OBJECTIVES

2.5.1 Hypotheses

1. Starch-lipid complexes containing amylose-lipid complexes produced from wet heat processing of maize starch with stearic acid or monoglyceride will be similar to fat-like material, for example, oil in terms of its sensory and lubrication properties.

Amylose-lipid complexes are formed when starch is pasted in the presence of lipids (D'Silva *et al.*, 2011; Wokadala *et al.*, 2012; Maphalla & Emmambux, 2016). The formation of amylose-lipid complexes makes amylose less available for junction zone formation and molecular entanglement (Saha & Bhattacharya, 2010). This will result in weaker gel network formation; hence, a resultant non-gelling material (D'Silva *et al.*, 2011). Amylose-lipid complexes formed are at nanoscale (Cuthbert *et al.*, 2017) hence will have an increased volume to surface area ratio. Thus the complexes will be more available to act as a layer of lubricant to provide an effective barrier to reduce asperity during oral processing. This will reduce friction and thus increase lubricating effect which will enhance the sensory perception of fat-related attributes such as fattiness, creaminess, smoothness and slipperiness (Malone *et al.*, 2003; Stokes, Boehm & Baier, 2013).

2. Substituting sunflower oil with different levels (0, 50, 80, and 98 %) of fat replacers as maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride in the formulation of reduced-fat mayonnaise-type emulsions will affect the quality characteristics in various ways;

- There will be a progressive increase in the aroma and initial flavour perception intensity of the reduced-fat mayonnaise-type emulsion with a decreased sustained flavour during consumption.

Reducing the concentration of oil in an oil-in-water emulsion will reduce the binding of non-polar volatile flavour compounds to oil in the matrix. This would increase the presence of non-polar volatile compounds in the headspace of the product (perceived as orthonasal aroma) as well as higher fractions of polar and non-polar flavour volatiles in the aqueous phase (Malone & Appelqvist, 2003) perceived as more intense retronasal aroma (part of flavour perception) during consumption of the product. This may be perceived as an imbalance of the flavour profile

(Overbosch, Afterof & Haring, 1991; Shamil, Wyeth & Kilcast, 1991; Doyen, Carey & Linforth, 2001). The amylose-lipid complex, as a fat replacer will form a ternary co-inclusion complex with the aroma compounds present in the mayonnaise-type emulsions thus reducing the overall aroma intensity (Tapanapunnitikul, Chaiseri, Peterson & Thompson, 2008).

- Textural properties (firmness, adhesiveness and viscosity) and lubricating properties of the reduced-fat mayonnaise-type emulsions will be similar to that of full fat mayonnaise, thus in-mouth perception of fattiness and creaminess will be similar as the lipid modified starches will act as a fat replacer.

Texture and mouthfeel play critical roles in product acceptability (Stokes *et al.*, 2013). Reducing the fat concentration of an oil-in-water emulsion decreases the viscosity (McClements & Demetriades, 1998) and reduces the oil coating on the oral mucosa and hence reduce coalescence during oral processing (Malone *et al.*, 2003). However, the addition of stearic acid modified maize starch at 50, and 80 % oil replacement increased the viscosity of low-calorie mayonnaise and also decreased the oil droplet size of low-calorie mayonnaise (Teklehaimanot *et al.*, 2013). The nano-sized particles of the lipid-modified starches as fat replacers (Zabar et al., 2009; Cuthbert *et al.*, 2017) will be effective in lubricating the oral cavity by reducing friction (Chen & Liu, 2006; Wu et al., 2007; Padgurskas *et al.*, 2013). This would be translated into an increase in the perception of fat-related attributes such as fattiness and creaminess (Dresselhuis *et al.*, 2008).

- The overall appearance (opacity, gloss, colour and homogeneity) of the reduced-fat mayonnaise-type emulsions will improve with increasing levels of fat replacement.

The opacity or lightness ($L*$) of an emulsion increases with increasing droplet concentration due to multiple scattering of light backwards (McClements, 2005). The chromaticity of the emulsions, on the other hand, decrease with increasing droplet concentration due to increased absorption of light (Chantrapornchai *et al.*, 2000). Also, as the droplet radius or size is increased, more light is scattered in the forward direction, implying less backward scattering (McClements, 2005). However, the addition of stearic acid modified maize starch in the production of low-calorie mayonnaise showed smaller oil droplets size compared to full-fat mayonnaise (Teklehaimanot *et al.*, 2013). Therefore, the addition of the lipid-modified starch will increase multiple backward scattering of light resulting in an emulsion with maximum lightness and minimum chromaticity.

3. The sensory shelf life of reduced-fat mayonnaise-type emulsions will not be affected as a function of substitution levels (0, 80, and 98 %) of lipid-modified maize starches (maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride) as fat replacers.

Mayonnaise is susceptible to chemical spoilage mainly through auto-oxidation of the fatty acids present in the vegetable oil used in the formulation (Depree & Savage, 2001). The rate of lipid oxidation in emulsion is influenced by the chemical structure of lipids, oxygen concentration, transition metal, droplet characteristics, and emulsion droplet interfacial properties (Waraho *et al.*, 2011). However, biopolymers such as polysaccharides (xanthan gum, gum Arabic, high and low methoxyl pectin, and methyl linoleate), have the ability to inhibit lipid oxidation in oil-in-water emulsions (Waraho *et al.*, 2011). Polysaccharides have a free radical scavenging effect (Matsumura *et al.*, 2003), the ability to bind with transition metal (McClements & Decker, 2000) and have metal ion-chelating ability (Shimada, Fujikawa, Yahara & Nakamura, 1992) that inhibit lipid oxidation. Polysaccharides also increase the viscosity of the aqueous phase and inhibit oxygen diffusion and movement of oil droplets, thus reducing their collision probability (Paraskevopoulou *et al.*, 2007). Therefore, the addition of the lipid-modified starches, as a biopolymer, will help retard the rate of lipid oxidation in the reduced-fat mayonnaise-type emulsions.

2.5.2 Objectives

1. To determine the effect of modifying maize starch with stearic acid, or monoglyceride on the sensory profile, tribological, and rheological properties of resultant starch-lipid complexes produced with the aim of producing fat replacers with fat-like properties.

2. To determine the effect of substituting sunflower oil with two starch-based fat replacers (maize starch + 1.5 % stearic acid, and maize starch + 2 % monoglyceride) at different substitution levels (0, 50, 80, and 98 %) on the rheological, lubricating and descriptive sensory properties of reduced-fat mayonnaise-type emulsions with the aim of producing reduced-fat mayonnaise with similar sensory properties as the full-fat counterpart.

3. To determine the effect of substituting sunflower oil with lipid-modified maize starches as fat replacers on accelerated (40 °C with 24 h fluorescent illumination) sensory shelf

life, physicochemical, and consumer acceptance of the mayonnaise-type emulsions with the aim of producing a shelf-stable and consumer acceptable reduced-fat emulsions to help address the global challenge of obesity.

3.0 RESEARCH

3.1 SENSORY, TRIBOLOGICAL, AND RHEOLOGICAL PROFILING OF ‘CLEAN LABEL’ STARCH-LIPID COMPLEXES AS FAT REPLACERS

Abstract

Dietary fat is highlighted as one of the critical risk factors that contribute to several chronic diseases. In this study, the sensory profile, tribological, and rheological properties of starch-lipid complexes, as a potential fat replacer, was investigated. Starch-lipid complexes were formulated by incorporating food-friendly chemicals (stearic acid and monoglyceride) into maize starch by wet-heat processing and compared with a commercial fat replacer. The starch-lipid complexes had good lubricating properties and were described by the panellists as being glossy, smooth, creamy and easy-to-swallow. All the complexes exhibited a shear thinning behaviour and had lower firmness, due to their non-gelling ability compared to the commercial fat replacer. The properties of starch-lipid complexes for non-gelling, good lubricating, smooth and creamy can be related to the formation of amylose-lipid complexes and other properties. The complexes have the potential to produce non-gelling emulsions having a creamy and smooth texture with no adverse effect on the overall aroma and flavour.

This phase of the study has been published:

Agyei-Amponsah J.[1], Macakova L.[2], DeKock H.L.[1], Emmambux M.N.[1] Sensory, triological, and rheological profiling of ‘clean label’ starch-lipid complexes as fat replacers, *Starch-Stärke*,

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3.1.1 Introduction

Urbanisation and the pursuit of convenient foods have shifted dietary preferences from nutrient-dense towards foods with high fat, refined carbohydrates and low–fibre (WHO, 2003; Kearney, 2010). Dietary fat has been highlighted as one of the critical risk factors that contribute to a number of chronic diseases, such as cardiovascular diseases, type 2 diabetes, obesity, and cancer (Krauss, Eckel, Howard, Appel, Daniels, Deckelbaum, Erdman, Kris-Etherton, Goldberg & Kotchen, 2000; Siri-Tarino *et al*., 2010; Mozaffarian, 2016). Therefore reducing fat content is recommended in food product innovation (Ma & Boye, 2013; McClements, 2015). Noteworthy, consumers who wish to change their diet to a reduced-fat regime often look for food products with minimal to no fat but with good sensory attributes.

Fat confers desirable sensory characteristics such as creaminess, aroma, palatability, texture, and lubricity in food (Rios, Pessanha, Almeida, Viana & Lannes, 2014) and generally improve the mouthfeel of food (Peng & Yao, 2017). Fat also affects the physical properties of products. For instance, in products such as chocolates, the presence of fat affects the melting, solidification, snap, appearance, fat bloom, and viscosity of the chocolate. In emulsions, functionalities such as melting, solidification, stability, and viscosity are all affected by the presence of fat (Rajah, 2002). It is therefore critical that the qualities that fat confers on food must be replaced when fat is removed.

Fat replacers are ingredients that can be added to reduced-fat foods to provide them with some qualities of fat (Ognean *et al*., 2006). Fat replacers are generally categorized into two groups, fat substitutes, and fat mimetics. Fat substitutes are mainly produced from lipid-based ingredients, and they chemically resemble lipids. Fat mimetics are protein or carbohydrate-based ingredients, and they imitate the sensory or physical properties of triglycerides (Roller & Jones, 1996; Akoh, 1998; Ognean *et al.*, 2006).

Carbohydrate-based fat replacers replace fat in reduced-fat foods either by mimicking fat particles in a particulate form or by contributing some other textural characteristics that would usually be found in full-fat foods (Peng & Yao, 2017). They function primarily to give body, increase viscosity, and to provide a creamy, slippery mouthfeel similar to that of fat (Akoh, 1998; Zoulias, Oreopoulou & Tzia, 2002). Carbohydrate-based fat replacers also can stabilise substantial quantities of water in a gel-like matrix, resulting in lubricating and flow properties similar to those of fats (Lucca & Tepper, 1994).

Stearic acid and monoglycerides are food-friendly chemicals that are used to modify starches to obtain 'clean' label modified starches (Maphalla & Emmambux, 2016). These lipids form complexes with amylose, known as amylose-lipid complexes with the hydrocarbon portion of the lipids inserted into the helical cavity of amylose (Becker, Hill & Mitchell, 2001; Putseys *et al*., 2010; López *et al*., 2012).

Starch-lipid complexes have some desirable functionalities in food systems. Singh and Byars (2009) reported no occurrence of syneresis in yoghurt samples stored at 4 °C when starch-lipid composites were used to replace milk solids in the production of low-fat yoghurts. Modification of maize and teff starches with stearic acid reduced the process of retrogradation in the resultant paste during cooling and storage (D'Silva *et al*., 2011). The enclosed lipid molecules in the form of amylose-lipid complexes, contribute to the stability of the amylose helix conformation by restricting the mobility of amylose (Lebail, Buleon, Shiftan & Marchessault, 2000; Zhou, Robards, Helliwell & Blanchard, 2007) and thus prevents the amylose from getting involved in retrogradation (Singh & Byars, 2009). Amylose-lipid complexes have been classified as part of the resistant starch fraction and do have similar health benefits as dietary fibre (Crowe, Seligman & Copeland, 2000; Tufvesson et al., 2003a). This is because complexes that are formed are less easily degraded by α-amylase enzymes (Eliasson & Krog, 1985).

Some studies have proposed the use of starch-lipid complexes as food additives in low-fat foods due to their ability to increase viscosity, add flavour and improve texture (Singh & Kim, 2009) and also for their high paste viscosity and non-gelling properties (D'Silva *et al*., 2011). Teklehaimanot *et al*. (2013) reported the potential of maize and teff starches modified with 1.5 % stearic acid as fat replacer after incorporating them into the production of low-calorie mayonnaise type emulsions. This potential may be due to the presence of amylose-lipid complexes as nanoparticles in these starches after the modification at the molecular level (Cuthbert *et al*., 2017). However, in these investigations, the tribological and sensory properties of these complexes on their own, as food ingredients providing specific product properties have not been researched. Thus the objective of this study was to determine the sensory, tribological, rheological profiles of starch-lipid complexes produced from ’food friendly’ chemicals; maize starch, stearic acid, and monoglycerides.

3.1.2 Materials and methods

3.1.2.1 Materials

Commercial white maize starch and pre-gelatinized maize starch (Amyral©) (both were, less than 10 % moisture, and about 25 % amylose on starch basis) were obtained from Tongaat Hullet® (Edenvale, South Africa). The proximate composition of the commercial Amyral© was approximately 112 g/kg moisture; 4.5 and 1.5 g/kg (db) protein and crude fat, respectively; and 250 g/kg amylose on a starch basis. Stearic acid (CAS No: 57-11-4) and glycerol monostearate [> 90 % distilled monoglyceride (CAS No: 31566-31-1)], the monoglyceride used in the study, were obtained from Merck (Pty) Ltd. (Modderfontein, South Africa) and Danisco (now DuPont, Grindsted, Denmark), respectively. A commercial citrus-base fat replacer (1.10 % total fat) was provided by Danlink Ingredients (Pty) Ltd. (Johannesburg, South Africa). Sunflower oil was obtained from a local supermarket.

3.1.2.2 Modification of maize starch

Modified maize starches were prepared by incorporating stearic acid or monoglyceride, into maize starch according to the method by D’Silva *et al.* (2011). Stearic acid and monoglyceride were dissolved in absolute ethanol in a beaker and added to the maize starch at 1.5 % and 2 % (w/w) respectively [based on recommendations by Maphalla and Emmambux (2016) and D’Silva *et al.* (2011). Maize starch + monoglyceride or maize starch + stearic acid samples were added to the ethanol in a 1:3 (w: v) starch: ethanol ratio and placed in a shaking water bath at 50 °C for 30 min to ensure complete mixing and incorporation of ingredients. The ethanol was then evaporated in an oven at 40 °C because it only served as a solvent for the solutes (maize starch, monoglyceride and stearic acid). Suspensions (10 % w/w) of the stearic acid-starch and monoglyceride-starch mixtures were pasted using a reactor (IKA® LR 1000 control, Staufen, Germany) at 91°C for 30 min at a stirring rate of 150 rpm.

3.1.2.3. Sensory evaluation

Ethical approval for this study was obtained from the ethics committee of the Faculty of Natural and Agricultural Sciences, University of Pretoria, South Africa (EC170425-111). Descriptive sensory valuation was conducted by a 9 member trained panel. Panellists were screened and selected using a series of acuity and discrimination tests [ISO 8586–1: 1993(E)], availability and willingness to participate in the study. Four samples (pasted maize starch + 1.5 % stearic acid, pasted maize starch + 2 % monoglyceride, commercial citrus-based fat replacer, and sunflower oil) were presented, and panellists were asked to generate terms describing the differences in products' sensory characteristics. This was followed by training sessions involving definition and agreement on the generated terms, references, and the use of Compusense Cloud (Compusense Inc., Guelph, Canada) for scaling the intensity of perceived characteristics. A total of 17 descriptors were developed and agreed upon by panel consensus (Table 3.1.1).

The commercial fat replacer was prepared according to the product specifications, that is 1:9 sample: water (w: v) mixed to a uniform consistency. Starch-lipid complexes, commercial fat replacer and sunflower oil, were placed in a water bath (35 °C – 40 °C) to attain uniformity in temperature. Sunflower oil was used as a control in anticipation of replacing sunflower oil with the starch-lipid complexes in a mayonnaise type emulsion in subsequent research. Samples (2 ml) were presented monadically in ramekins, labelled with randomly selected three-digit codes. Stainless steel teaspoons were provided for tasting the samples. Panellists cleansed their palates by eating fresh carrot rings and rinsing with warm water (40 °C – 45 °C) before and between evaluating each sample.

Table 3.1.1. Attributes and definitions for sensory profiling of fat replacer samples (maize starch + 1.5 % stearic acid, maize starch + 2 % monoglyceride, a commercial fat replacer, and sunflower oil)

Attributes	***Definitions***	***Anchors***
Appearance		
Glossy	Amount of gloss reflected from the samples	Not glossy – very glossy
Transparency	The degree to which the product looks transparent, ranging from cloudy to transparent	Not transparent – very transparent
Yell Yellowness	The intensity of the yellow colour from not yellow to very yellow	Not yellow – very yellow
Aroma		
Over-all aroma	Intensity of the aroma of the sample	No aroma - very intense aroma
Starchy aroma	The aroma associated with cooked maize starch	Not starchy - very starchy
Oily aroma	The aroma associated with vegetable oil	Not oily – very oily
Flavour		
Over-all flavour	Intensity of the flavour of the ingested sample	No flavour – very intense flavour
Astringency	Dry and puckering sensation in the mouth caused by substances such as tannins	Not astringent – very astringent
Bitterness	The basic bitter taste of which caffeine in water is typical	Not bitter – very bitter
Oily	The flavour associated with vegetable oil	Not oily – very oily
Metallic	A mouthfeel associated with tin cans or aluminium foil, a flat chemical feeling stimulated on the tongue by metals	Not metallic – very metallic
Texture (In-mouthfeel)		
Stickiness	Force required to remove the material that adheres to the palate	Not sticky – very sticky
Smoothness	Degree of smoothness perceived in the mouth Double cream plain yoghurt is an example of very smooth and semolina porridge an example of not smooth.	Not smooth – very smooth
Viscosity	The thickness or thinness of a sample being moved in the mouth. Evaluated prior to swallowing	Not viscous – very viscous
Creaminess	Degree of creaminess perceived in the mouth. Example of very creamy being full-fat yoghurt	Not creamy – very creamy
Mouth-coating	Residual coating covering mouth after swallowing the sample	No mouth-coating – presence of a mouth-coating layer
Firmness	Force required to compress a sample between the tongue and palate	Not firm – very firm
Jelly-like	A product with a soft elastic consistency and has the ability to wiggle due to the presence of gelatin.	Not jelly-like – very jelly-like
Easy-to-swallow	The amount of effort required to swallow the sample	Not easy to swallow – very easy to swallow

3.1.2.4 Tribology measurements (friction coefficient)

Tribology measurements were performed with a Mini-Traction Machine MTM2 (PCS Instruments Ltd., London, UK), using an elastomeric tribo-pair made of polydimethylsiloxane (PDMS), disk and ball, to mimic the soft nature of the oral surfaces of interest, i.e. tongue and palate (Bongaerts, Fourtouni & Stokes, 2007). The instrument was coupled to an external water bath, keeping the temperature in the measurements chamber at 35 ± 1°C during the experiments. A load of 2 N was applied in all experiments while sliding to rolling ratio (SRR), was set to 50 % to mimic the relative movement of the tongue and soft palate in the oral cavity, which has both sliding and rolling components.

For each sample, two tribological measurements were done while using a new PDMS tribo-pair, i.e. a new ball, and a new disk, each time. Samples (15 g) were poured into the measurement chamber onto the disk. The ball and the disk were brought into a loaded contact, and the entrainment speed was ramped from 750 mm/s to 1 mm/s and then back to 750 mm/s, while friction was accessed at 40 logarithmically spaced speeds during each ramp. Three ramping cycles immediately after each other were performed. The results for each speed are presented as an average of six friction coefficient values obtained during the three down-speed and the three up-speed ramps.

3.1.2.5 Flow property measurement

Flow properties of starch pastes were determined according to D'Silva *et al.* (2011) with modifications. Samples were collected at the end of the wet heat processing (pasting) phase and the shear behaviour determined with a Physica MCR 101 Rheometer (Anton Paar, Ostfildern, Austria) using a vane and cup. The shear rate was increased from; 0.01/s to 1000/s and reduced back from 1000/s to 0.01/s at 25 °C. The data collected upon increased shear rate were fitted to the Power law equation, $\delta = K\dot{\gamma}n,$ where δ is the shear stress measured in Pascal (Pa) and $\dot{\gamma}$ is the shear rate (s_{-1}). K is the consistency coefficient (Pas^n), and n is the flow behaviour index, respectively.

3.1.2.6 Texture measurements

The textural characteristics of all the samples were analyzed as described by Bultosa and Taylor (2004). Starch pastes were hot-filled into polypropylene containers (16 mm height x 37 mm diameter) and stored at 23 °C for 24 h to allow for proper network formation on cooling. Paste firmness and adhesiveness were analysed using an EZ-test texture analyser (EZ– L, Shimadzu Tokyo, Japan) with a P/20p cylinder probe (20 mm diameter). Pastes were compressed 5 mm at a speed of 2 mm/s at 25 °C, and then the probe was retracted from the sample.

Firmness was determined as the peak height corresponding to the maximum force of compression. Adhesiveness (the force required to retract the probe from the sample) was measured as the area of the curve during retraction of the probe.

3.1.2.7 Thermal properties

The thermal properties of the freeze-dried starch paste obtained after pasting were determined according to the method described by Wokadala *et al*. (2012) with some modifications using a high-pressure Differential Scanning Calorimetry (DSC) system, HP DSC827e, Mettler Toledo (Greifensee, Switzerland). Starch pastes obtained after pasting at 91 °C for 30 min in the reactor were immediately frozen at -20 °C and freeze-dried at -40 ºC for 5 days. The freeze-dried starch powder (10 mg dry basis) was mixed with distilled water (30 mg) and then equilibrated for 24 h at about 23 ± 1 °C for DSC analysis. Scanning was done from 25 °C to 170 °C under pressure (4 MPa) using N_2 at a rate of 10 °C/min. Indium (Tp = 156.6 °C, 28.45 J g^{-1}) was used as a standard to calibrate the DSC, and an empty pan served as a reference.

3.1.2.8 Statistical analysis

A one-way analysis of variance (ANOVA) and Fisher least significant difference test at $P \leq 0.05$ were used to establish the effect of the different samples (pasted maize starch + 1.5 % stearic acid, pasted maize starch + 2 % monoglyceride, pre-gelatinized maize starch and commercial fat replacer) on textural and rheological properties (firmness, adhesiveness, and n & K values). An Independent Samples t-Test was performed on the DSC results to compare the means of the two independent groups (pasted maize starch with 1.5 % stearic acid and pasted maize starch with 2 % monoglyceride) to determine the significance of variance between the means. Each sample was sampled and analyzed three times for their thermal properties. Statistical analysis was performed using IBM SPSS version 20 (SPSS, Inc., 1998, Chicago, IL). Two way ANOVA was used to reveal the significant effect of the different sensory descriptors on the samples using XLSTAT 2014. Principal component analysis (PCA) using a covariance matrix (cov-PCA) was done on average scores for the sensory attributes over four evaluation sessions to map out the variances among the samples.

3.1.3 Results

3.1.3.1 Sensory evaluation

Table 3.1.2 shows the analysis of variance of 19 sensory descriptors of the different fat replacers (Maize starch +1.5 % stearic acid, maize starch + 2 % monoglyceride, commercial fat replacer, and sunflower oil). Sunflower oil was used as a control in anticipation of replacing sunflower oil with the starch-lipid complexes in a food product, for example, mayonnaise with reduced oil. Pregelatinized maize starch was not included in the sensory evaluation because samples gelled during storage at 35 to 40°C. This makes it unsuitable to be used as a replacement for sunflower oil as it will produce a gelled mayonnaise type emulsion.

The overall aroma intensity of maize starch with 1.5 % stearic acid and maize starch with 2 % monoglyceride was significantly ($p < 0.05$) lower compared to the commercial fat replacer (Table 3.1.2). The oily aroma intensity of the maize starch with stearic acid and maize starch with monoglyceride pastes as well as the commercial fat replacer were all rated significantly ($p < 0.05$) lower compared to sunflower oil. The overall flavour of the starch-lipid complexes was rated significantly less intense ($p < 0.05$) compared to sunflower oil and the commercial fat replacer.

The starch-lipid complexes were rated significantly ($p < 0.05$) more transparent than the commercial fat replacer but significantly less transparent than sunflower oil. The starch-lipid complexes exhibited the characteristic glossy appearance of pasted maize starch and hence were rated significantly more glossy (8.0 to 8.7) than the commercial fat replacer (1.5) which had a rather dull opaque appearance (visual observation). Panellists also rated the starch-lipid complexes significantly less bitter ($p < 0.05$) compared to the commercial fat replacer.

Panellist generally rated the two starch-lipid complexes high for their in-mouth attributes such as smoothness, creaminess, and easy-to-swallow compared to the commercial fat replacer. The smoothness of the starch-lipid complexes was rated similar to sunflower oil. Although the starch lipid complexes were distinctively more jelly-like and presented a more sticky mouthfeel compared to the sunflower oil, they were rated significantly ($p < 0.05$) more creamy than oil and the commercial fat replacer. The commercial fat replacer was however scored significantly ($p < 0.05$) high for stickiness.

Table 3.1.2. Descriptive profiling (means ± standard deviations) of the sensory properties# of modified starch pastes and a commercial fat replacer as replacers for sunflower oil

Samples / Attributes	*Maize starch MS+ 2 % monoglyceride MG*	*Maize starch MS+ 1.5 % stearic acid SA*	*Commercial fat replacer**	*Sunflower oil (standard)*
Overall aroma	$4.0^{b} \pm 2.7$	$4.8^{b} \pm 3.3$	$8.1^{a} \pm 2.5$	$4.2^{b} \pm 3.1$
Oily aroma	$1.2^{b} \pm 2.6$	$1.1^{b} \pm 2.5$	$1.2^{b} \pm 2.8$	$7.9^{a} \pm 2.7$
Starchy aroma	$4.4^{b} \pm 3.5$	$5.2^{b} \pm 3.8$	$7.7^{a} \pm 3.0$	$0.2^{c} \pm 0.7$
Transparency	$1.7^{b} \pm 3.1$	$1.8^{b} \pm 3.3$	$0.2^{c} \pm 1.5$	$9.6^{a} \pm 1.1$
Glossy	$8.7^{b} \pm 2.3$	$8.0^{b} \pm 2.8$	$1.5^{c} \pm 2.1$	$9.8^{a} \pm 0.3$
Yellowness	$0.0^{b} \pm 0.0$	$0.0^{b} \pm 0.1$	$5.2^{a} \pm 2.6$	$5.6^{a} \pm 2.8$
Overall flavour	$2.4^{c} \pm 2.6$	$2.6^{c} \pm 3.0$	$7.0^{a} \pm 3.4$	$5.4^{b} \pm 3.6$
Bitterness	$1.7^{b} \pm 3.3$	$1.9^{b} \pm 3.6$	$8.8^{a} \pm 2.8$	$0.9^{b} \pm 2.3$
Oily	$1.7^{b} \pm 3.1$	$1.7^{b} \pm 3.3$	$2.1^{b} \pm 3.5$	$9.8^{a} \pm 0.4$
Metalic flavour	$3.4^{a} \pm 3.2$	$3.3^{a} \pm 3.3$	$4.5^{a} \pm 3.9$	$0.9^{b} \pm 2.3$
Astringent	$3.0^{b} \pm 3.7$	$3.2^{ab} \pm 4.0$	$4.8^{a} \pm 4.3$	$1.0^{c} \pm 2.6$
Smoothness	$8.7^{a} \pm 1.6$	$8.9^{a} \pm 2.4$	$5.0^{b} \pm 3.0$	$8.8^{a} \pm 2.9$
Jelly-like	$7.9^{a} \pm 2.9$	$5.8^{b} \pm 3.7$	$0.0^{c} \pm 0.1$	$0.8^{c} \pm 2.5$
Creaminess	$4.6^{a} \pm 3.7$	$5.7^{a} \pm 3.7$	$3.0^{b} \pm 3.6$	$2.3^{b} \pm 3.7$
Stickiness	$3.7^{b} \pm 3.5$	$4.7^{b} \pm 3.8$	$6.3^{a} \pm 4.0$	$0.0^{c} \pm 0.1$
Mouth-coating	$2.8^{b} \pm 3.4$	$3.6^{b} \pm 3.9$	$6.9^{a} \pm 3.8$	$2.8^{b} \pm 3.7$
Viscosity	$2.9^{b} \pm 3.1$	$2.6^{b} \pm 3.1$	$2.9^{b} \pm 3.8$	$6.0^{a} \pm 4.4$
Easy-to-swallow	$7.2^{b} \pm 3.0$	$6.8^{b} \pm 3.5$	$3.8^{c} \pm 3.6$	$8.8^{a} \pm 2.5$
Firmness	$3.3^{b} \pm 3.0$	$3.3^{b} \pm 3.4$	$6.3^{a} \pm 3.8$	$0.5^{c} \pm 2.1$

a) Mean values in the same rows with different superscripts differ significantly ($p < 0.05$)
b) # Refer to Table 3.1.1 for definitions of the sensory properties and scale characteristics (1 = property not present; 9 = property present at a very intense level)
c)* a citrus based commercial fat replacer

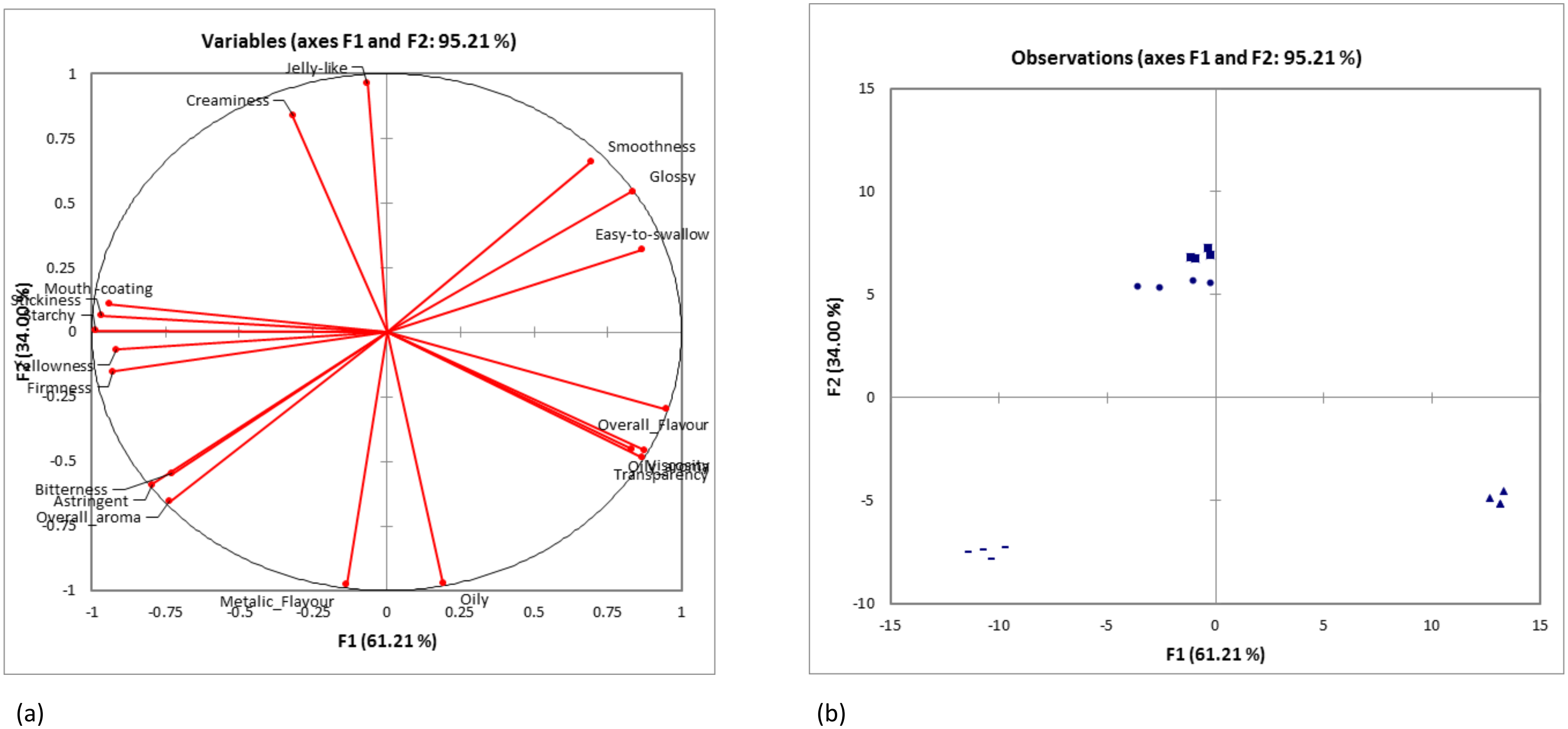

Figure 3.1.1. Covariance principal component analysis (cov-PCA) plots for sensory profiles of starch-lipid complexes, commercial fat replacer and sunflower oil as evaluated during four replicate sessions. (a) PC 1 and 2 map showing loadings of descriptors; (b) score plot showing loadings of samples

(▲) Sunflower oil, (■) Maize starch + 2 % monoglyceride, (•) Maize starch + 1.5 % stearic acid, (▬) commercial fat replacer

The principal component analysis (PCA) plots summarizing the sensory attributes for the starch lipid complexes, commercial fat replacer, and sunflower oil is shown in Figure 3.1.1. The first and second components together explained 95 % of the variation. PC1 explained 61 % of the total variance and PC2 accounted for the remaining 34 %.

3.1.3.2 Tribological properties

To understand the lubricating properties of the starch-lipid complexes, the commercial fat replacer, and pre-gelatinized maize starch, the friction coefficient of the samples when sheared between the tribo-pairs was plotted as a function of entrainment speed (Figure 3.1.2). The friction coefficient of all the samples reduced with increasing entrainment speed from the initial high values at the boundary regime to the mixed lubrication regimes. At the boundary regime, the starch-lipid complexes had a lower friction coefficient compared to the pre-gelatinized maize starch that recorded higher values of all the tested samples. The commercial fat replacer, on the other hand, recorded much lower friction coefficient values in both the boundary and mixed regimes. Tribological measurements, unlike the rheological measurements, was able to discriminate between the two starch-lipid complexes (Figure 3.1.2). The maize starch modified with 2 % monoglyceride had lower friction coefficient at the mixed regime compared to maize starch modified with 1.5 % stearic acid.

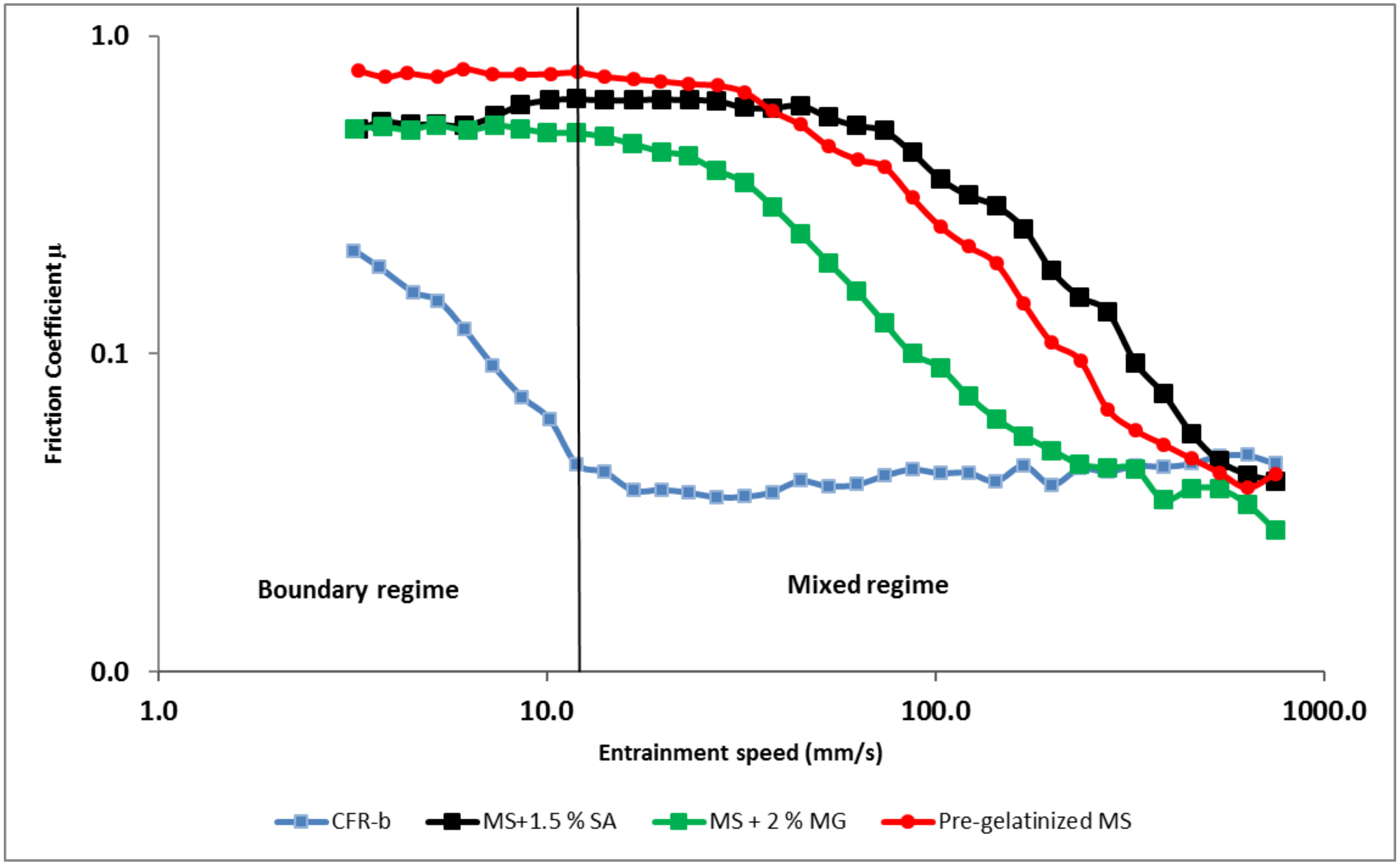

Figure 3.1.2. Tribological properties of maize starch modified with stearic acid and monoglyceride compared with a commercial fat replacer

CFR: Commercial fat replacer, FSA – Maize starch + 1.5 % Stearic acid, FMG – Maize starch + 2 % Monoglyceride

3.1.3.3 Rheological measurement

A graph of the viscosity of the two starch-lipid complexes, pre-gelatinized maize starch and a commercial fat replacer versus shear rate is shown in Figure 3.13. All four samples had their viscosities decreasing with increasing shear rate. Both starch-lipid complexes and pre-gelatinized maize starch exhibited zero shear viscosities while the commercial fat replacers showed no zero shear viscosity within the limit of measurement of 0.001 s-1(Figure 3.1.3). This implies that the modified starches, if included in products such as mayonnaise, could exhibit some positive initial resistance to deformation, unlike the commercial fat replacer that will easily flow to a small amount of applied shear.

All the samples had a flow behaviour index (n) less than 1 with values ranging between 0.2 and0.4. Flow behaviour index (n) recorded for the starch-lipid complexes were significantly lower ($p< 0.05$) compared to the pre-gelatinized starch and the commercial fat replacer. The consistency coefficient (K), like the zero shear viscosity, of the maize starch with 1.5 % stearic acid was significantly ($p < 0.05$) higher than that of maize starch with 2 % monoglyceride. However, consistencies of the two starch-lipid complexes were significantly ($p < 0.05$) lower compared to that of the commercial fat replacer. All samples had significantly different ($p < 0.05$) hysteresis areas (Table 3.1.3). Maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride had 86857 Pa s and 179893 Pa s respectively (Table 3.1.3). These hysteresis values were significantly lower ($p < 0.05$) than the value reported for the pre-gelatinized maize starch (225742 Pa s). A negative and higher hysteresis area of -329697 Pa s was observed for the commercial fat replacer as compared to the others that showed a positive hysteresis area.

Table 3.1.3 shows the texture properties of the starch-lipid complexes determined after 24 h storage at 23 ± 1 °C. Pre-gelatinized maize starch had the highest ($p < 0.05$) firmness of 3.5 N. This was followed by the commercial fat replacer with a firmness of 0.9 N. The maize starch modified with 2 % monoglyceride recorded a firmness of 0.8 N while the maize starch with 1.5 % stearic acid had a significantly ($p < 0.05$) lower firmness of 0.7 N. The pre-gelatinised starch was a gelled material; compared to the starch modified with stearic acid and monoglyceride, and the commercial fat replacer characterized as a thick and viscous paste. The commercial fat replacer had a significantly ($p < 0.05$) higher adhesiveness of -0.5 N compared to the two starch-lipid complexes that had adhesiveness of -0.2 N.

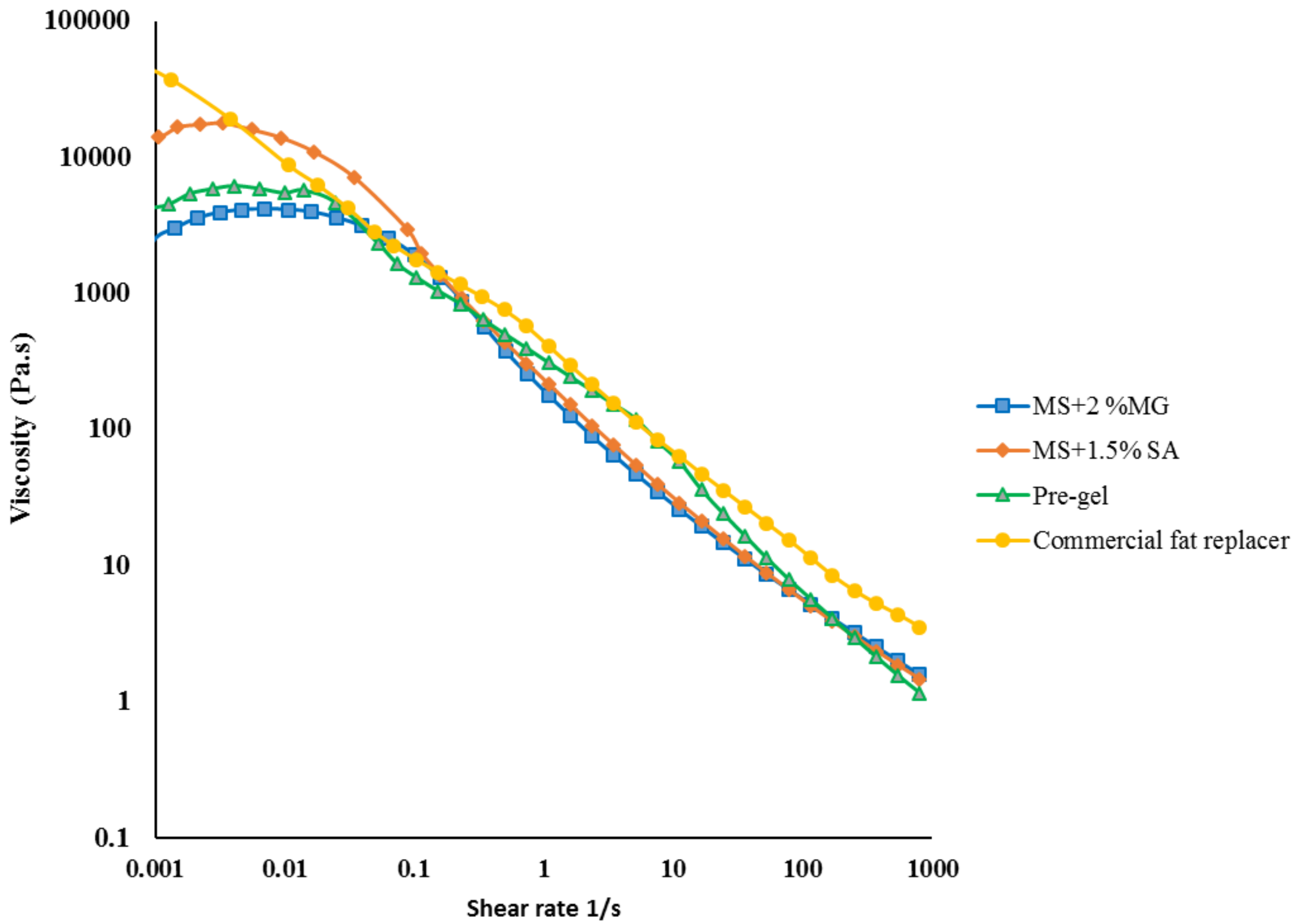

Figure 3.1.3. Effects of stearic acid and monoglyceride addition on the viscosity of maize starch compared with the viscosities of pre-gelatinized maize starch and a commercial fat replacer

MS – Maize starch, SA - Stearic acid, MG – Monoglyceride, Pre-gel – Pre-gelatinized maize starch

Table 3.1.3. Textural and flow-properties [consistency coefficient (K), flow behaviour index (n) and hysteresis] of different fat-replacers

Samples	***Zero shear viscosity (Pa.s)***	***n***	***K(Pa s^n)***	***Hysteresis (Pa s)***	***R^2***	***Firmness (N)***	***Adhesiveness (N)***
Pre-gelatinized maize starch	5956.7^b ± 168.6	0.4^c ± 0.0	196^b ± 14	225742^d ± 15307	0.8^b ±0.0	3.5^c ± 0.0	-0.2^b ± 0.0
MS+ 1.5 % SA	17666.7^c ± 1222.0	0.2^a ± 0.0	187^b ± 8.9	86857^b ± 8637	0.7^a ± 0.0	0.7^a ± 0.1	-0.2^b ± 0.0
MS + 2 % MG	4123.3^a ± 32.0	0.2^a ± 0.0	145^a ± 16	179893^c ± 13296	0.8^b ± 0.0	0.8^b ± 0.1	-0.2^b ± 0.0
Commercial fat replacer	-	0.4^c ± 0.0	305^c ± 14	-329697^a ±16286	0.9^c ± 0.0	0.9^b ± 0.1	-0.5^a ± 0.0
p-value	0.00	0.00	0.00	0.00	0.00	0.00	0.00

a) Values are means of triplicate readings with standard deviation
b) Mean values in the same column with different superscripts differ significantly ($p < 0.05$)
c) MS – Maize starch, SA - Stearic acid, MG – Monoglyceride
d) n and K values were calculated using the upward curve i.e. increasing shear rate from 0.1 to 800 s^{-1} and from the Power Law model

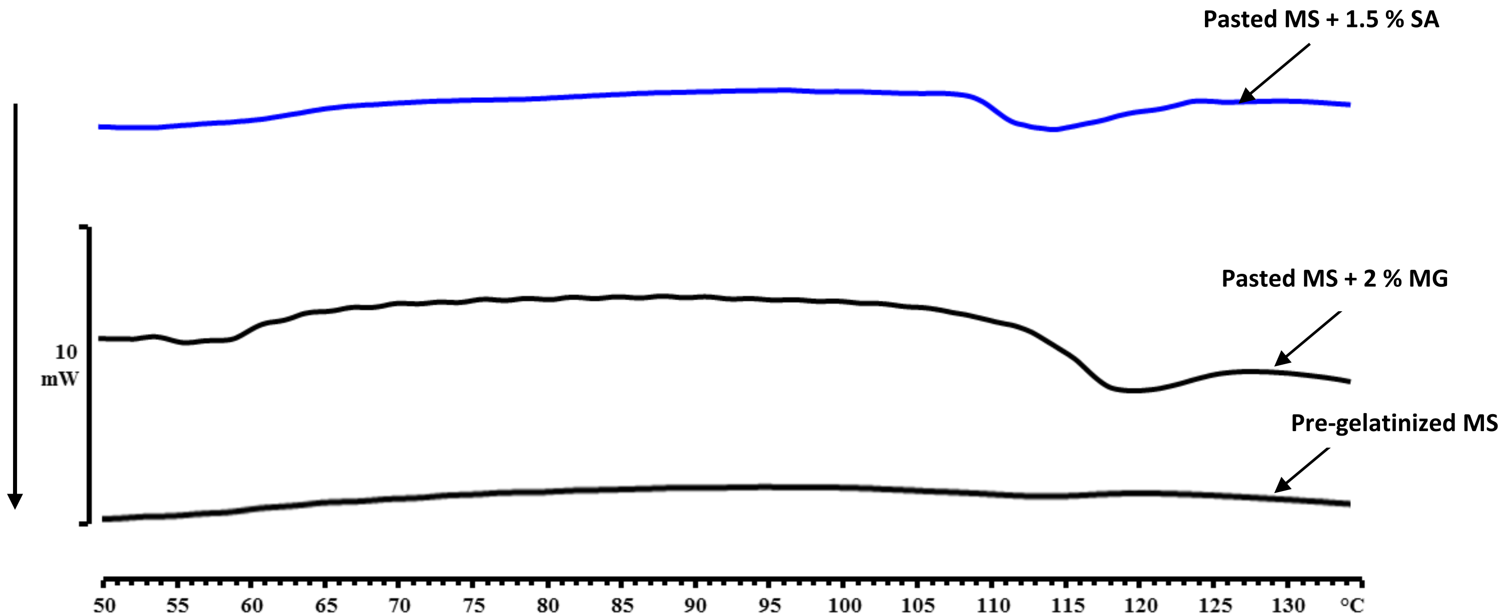

Figure 3.1.4. Thermal properties of maize starch modified with stearic acid and monoglyceride using a Differential Scanning Calorimetry (DSC)

- MS – Maize starch, SA – Stearic acid, MG – Monoglyceride

A transition endotherm attributed to the formation of amylose-lipid complexes (Putseys *et al.*, 2010), was observed for both starch-lipid complexes (Figure 3.1.4). Maize starch modified with 1.5 % stearic acid, had a transition temperature range of 108–123 ° C with an enthalpy ΔH of about 5 Jg^{-1} and maize starch modified with 2 % monoglyceride, had a transition temperature range of 114- 126 ° C with an enthalpy ΔH of 7 Jg^{-1}. From the statistical analysis, a two-tail significance of 0.067 was obtained. Implying that enthalpy differences recorded in the two samples were not significant ($p > 0.05$).

3.1.4 Discussion

The descriptive profiling of the different fat replacers and the sunflower oil showed that the starch lipid complexes were generally scored low for their overall aroma intensity. This could be due to the base constituents (maize starch, stearic acid & monoglyceride) used in producing the complexes as against that of the commercial fat replacer (citrus base). Amylose, as well as amylopectin, present in maize starch, is reported to have the ability to form complexes with many low-molecular-weight organic compounds, including aroma molecules (Arvisenet *et al.*, 2002; Jouquand, Ducruet & Le Bail, 2006). Therefore, it can be suggested that both amylose and amylopectin present in the maize starch possibly complexed with aroma compounds and reduced the overall aroma intensity. The release of aroma molecules from the food matrix to be perceived at the headspace of the food is governed mostly by interactions between food components and aroma compounds (Arvisenet *et al.*, 2002). Sunflower oil, on the other hand, is a triglyceride made up mainly of linoleic acid and oleic acid with small percentages of stearic acid and palmitic acid and is reported to have a slightly fatty aroma (Gunstone, 2002).

Both starch-lipid complexes were rated low for overall flavour. This is due to the bland or tasteless nature of cooked maize starch (BeMiller & Whistler, 2009). The commercial fat replacer (citrus-based), as expected, was scored higher for bitterness compared to the starch-lipid complexes. Bitter molecules are reported to occur in many variations, with the strongest and most important representatives found in certain alkaloids, terpenoids, and flavonoids (Ley, 2008). Citrus fruits naturally contain the flavonoid, naringin, which is responsible for the fruits bitter taste (Tripoli, La Guardia, Giammanco, Di Majo & Giammanco, 2007), and it is perceived in products that they are included in. From the PCA plot, PC1 effectively separated the commercial fat replacer from sunflower oil but placed the two newly formulated starch-lipid complexes centrally between the two. This may be due to the fat-like attributes associated with the starch-lipid complexes. The starch-lipid complexes were mainly associated with glossiness, creaminess, transparency, smoothness, easy-to-swallow, and jelly-like attributes. While the commercial fat-replacer, on the other hand, was described by the panel as more firm, more intense metallic flavour, yellowness, bitterness, overall flavour, astringency, mouth-coating, sticky and starchy aroma. The characteristic glossy appearance, smooth, creamy and easy-to-swallow mouthfeel and more subtle, blander overall aroma and flavour nature of the newly formulated starch-lipid complexes defined by the PCA plot, could potentially make these good fat-replacers and these properties could be transferred into products (e.g. mayonnaise) in that they are incorporated into.

Two lubricating regimes (boundary and mixed) were identified for the starch-lipid complexes from the Stribeck curve. At boundary regime, the two tribo-surfaces are in close contact and friction is dominated by physical contact of the surfaces, (Chen & Stokes, 2012) making it difficult for proper entrainment of starch paste samples that are expected to act as lubricants. However, the lower friction coefficient values recorded for the starch-lipid complexes compared to the pre-gelatinized starch could possibly be due to the nanoparticle sizes (2.4–6.7 nm) of the amylose-lipid complexes (Cuthbert *et al.*, 2017). The nanoparticle nature of the amylose-lipid complexes possibly increased the volume to surface area ratio of the complexes making them more available to act as a layer of lubricant to provide an effective barrier to reduce asperity between the tribo-surfaces. Hence the observed lowering of friction coefficient with increasing entrainment speed compared to uncomplexed maize starch.

The surprisingly lower friction coefficient values recorded for the commercial fat replacer can probably be due to the presence of 1.10 % total fat (information from product specification sheet), its high viscous (Figure 3.1.3) and adhesive nature (Table 3.1.3). These possibly made it more available to act as lubricants by preventing the two tribo-surfaces from being in close contact at the lower entrainment speed. The physical presence of polymer between the contact surfaces prevent them from coming together, and the high viscosity of the fluid causes suppression of turbulent flow and limits the drag force at the contact zone, hence reducing friction (Malone *et al.*, 2003).

Lower friction coefficient values observed for the starch-lipid complexes in the mixed regime (Figure 3.1.2) might have influenced the perceived smoothness, creaminess, and easy-to-swallow nature of the starch-lipid complexes by panellists. Lower friction coefficient implies increased lubricating effect which is reported to enhance the sensory perception of fat-related attributes such as fattiness, creaminess, and slipperiness (Malone *et al*., 2003; Stokes, Boehm & Baier, 2013).

Rheologically, all four tested samples (maize starch with 1.5 % stearic acid and maize starch with 2 % monoglyceride, a commercial fat replacer, and pre-gelatinised maize starch) are clearly Non-Newtonian and exhibit shear-thinning behaviour, i.e. their viscosity decreases with increasing shear rates. This phenomenon can be attributed to the breakdown of structural units in the starch paste due to hydrodynamic forces generated during shear (Rao, 2007) allowing starch molecules to freely align themselves in the direction of shear during measurement (BeMiller & Whistler, 2009). Che, Li, Wang, Özkan, Chen and Mao (2008), D'Silva *et al*. (2011) and Maphalla and Emmambux (2016) reported similar results for different starch pastes and their modified forms.

The starch-lipid complexes had lower values of flow behaviour index 'n', consistency coefficient, K, and hysteresis compared to the commercial fat replacer and the pre-gelatinized starch. This could possibly be attributed to the formation of amylose-lipid complexes during the modification process of maize starch with stearic acid and monoglyceride. Complexation occurs when the hydrophobic aliphatic fatty acid chain of the lipids goes to reside in the hydrophobic environment within the V-amylose helix through hydrophobic forces (Obiro, Sinha Ray & Emmambux, 2012). .Inside the cavity, the amylose-lipid interactions are stabilised by molecular hydrogen bonds and van der Waals forces between the amylose glucose residues, water molecules and the lipid (Nimz *et al*., 2004). The formation of amylose-lipid complexes prevents further aggregation of amylose double helix from forming crystalline structures that would strengthen the network formation in the paste. Amylose-lipid complexes are formed when starch is pasted in the presence of lipids (D'Silva et al., 2011; Wokadala et al., 2012; Maphalla & Emmambux, 2016). Available amylose molecules, after starch pasting, associate with each other to form junction zones through hydrogen bonds (BeMiller & Whistler, 2009; Saha & Bhattacharya, 2010). This causes the starch paste to form a stable gel through molecular entanglement. Limited junction zones formation in the amylose-lipid complexes, causes these starches to align more easily in the direction of shear compared to starches with extensive molecular entanglements that require more energy to disentangle and align in the direction of shear. The negative hysteresis value recorded for the commercial fat replacer could probably be indicative that the paste has some antithixotropic properties. Thixotropic suspensions exhibit time-dependent behaviour and given time, sheared systems will regain their original structure (Dewar & Joyce, 2006). During the process of shearing, there is a decrease in viscosity with time until a balance is reached between structural breakdown and reformation for thixotropic suspensions (Santos, Carignano & Campanella, 2017).

The possible formation of amylose-lipid complexes was confirmed by results obtained from DSC measurements. The transition temperature ranges obtained for both starch-lipid complexes is associated with the melting of crystalline amylose-lipid complex (type II) as reported by Raphaelides and Karkalas (1988) and Tufvesson, Wahlgren and Eliasson (2003b). Tufvesson *et al.* (2003b) reported a thermal transition temperature range of 115.3 – 123.2 °C when they pasted maize starch with glycerol monosterin. Similar transition temperature ranges (107.1 - 114.7 °C) were also reported by Wokadala *et al.* (2012) when they pasted maize starch with stearic acid. In both cases, researchers attributed these high values to the formation of Type II amylose-lipid complexes during prolong heating at high temperature.

Fatty acids with longer chain lengths (between 14C and 18C) and lower degree of unsaturation form thermal stable complexes (Gelders, Vanderstukken, Goesaert & Delcour, 2004; Putseys *et al.*, 2010). This is due to increased hydrophobic interactions that allow the long hydrocarbon chain of the fatty acid to protrude deeper into the helix cavity of the amylose and thus be stabilised largely (Tufvesson *et al*., 2003a, b; Putseys *et al.*, 2010). Thus, stearic acid, a saturated 18-Carbon chain fatty acid, form amylose-lipid complexes more readily compared to the monoglyceride that has a bulkier substituted carboxyl polar head. This could subject the monoglyceride to steric hindrance that might require a larger helix cavity (Putseys, Derde, Lamberts, Goesaert & Delcour, 2009) and prolong heat treatment at higher temperatures to complex (Tufvesson *et al.*, 2003a).

Amorphous type I V-amylose complexes are formed at a lower heating temperature at about 60 °C and dissociate between 95 and 105 °C, whilst a semi-crystalline type II V-amylose complexes are formed at about temperatures 90 °C and dissociate around 115 °C (Gelders *et al*., 2004;

Putseys *et al.*, 2010). Gelders *et al.* (2004) demonstrated the effect of temperature on complexation when they formed more of type I complexes at 60 °C and more type II complexes at 90 °C. In related research, Tufvesson *et al*. (2003a, 2003b) and Wokadala *et al.* (2012) reported that longer heat treatment favoured the formation of complex type II V-amylose relative to the formation of Type I, and described monoglycerides to easily form Type II complexes when heated for prolong period.

The non-significant difference in enthalpy values for the stearic acid and the monoglyceride complexes can be as a result of the concentration of the lipids (1.5 % stearic acid and 2 % monoglyceride) used. Tang and Copeland (2007) demonstrated that maximal complex formation occurs at a different concentration for different lipids, which is related to the water solubility and critical micellar concentration of the lipid. Another possible reason could be due to thermal annealing of the amylose-stearic acid complex and the amylose-monoglyceride complex during heating at 91 °C. Wokadala *et al.* (2012) suggested that Type I that contains randomly oriented amylose-lipid complex helices can covert to an organised Type II amylose-lipid complex helices when heated at high temperature (>90 °C).

In terms of sensory profiling, the formation of amylose-lipid complexes possibly contributed to the slight cloudiness observed by the panel. Hence the significantly lower transparency values recorded for the starch-lipid complexes compared to the sunflower oil. Formation of amylose-lipid complexes has been reported to reduce paste clarity (Bultosa & Taylor, 2004; D'Silva *et al.*, 2011). The commercial fat replacer, on the other hand, had a light yellow beige colour (information from product specification sheet), that gave it an opaque appearance after preparation.

The formation of amylose-lipid complexes, makes amylose less available for junction zone formation and molecular entanglement, resulting in weaker gel network formation. This enhanced the textural properties of the starch-lipid complexes as a potential fat replacer, by contributing to the reduction in the firmness of the starch-lipid complexes compared to the pre-gelatinized starch which had already gone through the retrogradation process to form the firm gel structure. Despite the sensory panellists rating the starch-lipid complexes very jelly-like, the samples were still flowable upon scooping and placing on the tongue, and this could be due to the non-gelling nature of starch-lipid complexes (D'Silva *et al.*, 2011).

Adhesiveness is the ability of starch gel to stick to other objects (Fiszman & Damasio, 2000), this implies that an increase in attractive force within the starch gel matrix will reduce the adhesion of starch gel to a measuring probe (Bultosa & Taylor, 2004). The lower adhesives values recorded for the starch-lipid complexes implies that there are stronger intermolecular forces within their matrix than in the commercial fat replacer. High stickiness scored by the panellist in the case of the commercial fat replacers is in agreement with its high adhesiveness measured instrumentally. Stickiness, as defined above for the sensory evaluation, is the force required to remove the material that adheres to the palate. This implies that the commercial fat replacer stuck more to the palate compared to the starch-lipid complexes, which can be said to have a greater attractive force within its starch gel matrix (Bultosa & Taylor, 2004).

3.1.5 Conclusions

Maize starch modified with either stearic acid or monoglyceride and pasted has the potential to be used as fat replacers, to produce non-gelling emulsions that will have a creamy and smooth texture with little effect on the aroma and flavour of the final product. The sensory, tribological and rheological profile of two starch-lipid complexes has been established. The starch lipid complexes exhibit fat-like properties such as being glossy, creamy, smooth, transparent with mouth-coating properties similar to oil that can aid easy swallowing. They are less firm, paste-like and show better lubricating properties compared to the gelled nature of the pre-gelatinized maize starch. In follow up research, the application in low-fat mayonnaise and effect on the sensory profile, consumer acceptance, and shelf life will be explored.

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3.2 EFFECT OF SUBSTITUTING SUNFLOWER OIL WITH FAT REPLACERS ON SENSORY PROFILE, TRIBOLOGY AND RHEOLOGY OF REDUCED-FAT MAYONNAISE-TYPE EMULSIONS

Abstract

Reduction of the fat content of popular food products, in an attempt to reduce fat intake but without compromising the desirable sensory properties provided by fat is a challenging task. Due to the multiple roles played by fat for the sensory quality of foods, some products formulated with fat replacers do not compare favourably to their full-fat counterparts. The fat replacers containing amylose-lipid complexes, maize starch with 1.5 % stearic acid and maize starch with 2 % monoglyceride, were used to formulate reduced-fat mayonnaise-type emulsions at 0 % (full-fat control), 50 %, 80 % and 98 % level of oil replacement. Reduced-fat emulsions containing starch/monoglyceride were rated similar ($p > 0.05$) to the full-fat mayonnaise at all the oil replacement levels in terms of smoothness, creaminess, melting and mouth-coating. They also had similarities in terms of thickness and easy-to-swallow sensory attributes, up to 50 % substitution level. For the corresponding starch/stearic acid emulsions, the smoothness, thickness, creaminess and mouth-coating attributes were rated lower while the melting and easy-to-swallow attributes were rated higher than for the starch/monoglyceride emulsions. The reduced-fat emulsions containing starch/stearic acid had lower zero shear viscosity and firmness and gave rise to higher friction in simulated conditions compared to the reduced-fat emulsion containing starch/monoglyceride and full-fat mayonnaise. The ability of the reduced-fat emulsions to support the highly viscous structure, provided by the presence of amylose-lipid complexes in the fat replacers were better for the starch/monoglyceride fat replacer than for the starch/stearic acid fat replacer.

3.2.1 Introduction

Diet and lifestyle changes have been related to the increased prevalence of diet-related non-communicable diseases (Vorster *et al*., 2013). Awareness of the adverse health effects associated with overconsumption of fat has led to the development of reduced-fat products in the food industry. However, fat present in most foods provides unique texture, flavour, and aroma to the food (McClements & Demetriades, 1998), which is difficult to achieve in the reduced-fat products that often fail to deliver an expected food experience (Devereux *et al.*, 2003; O'brien *et al*., 2003). Fat reduction through the use of fat replacers that would provide the desirable sensory properties would increase the acceptability of the reduced-fat products and contribute to a more balanced diet and well-being of the population.

In the formulation of low-fat emulsions, researchers employ non-fat ingredients such as starches, gums and proteins, to replace some quality attributes that are lost when fat is removed (McClements & Demetriades, 1998). These fat replacers are used to either physically mimic the properties of fat molecules or to adjust the sensory and rheological characteristics to match those of the full-fat product (Roller & Jones, 1996). Identifying the ideal fat replacer that can mimic the multi-functional roles played by fat in food emulsions remains a challenge for the food industry, and research is ongoing. Popular fat replacers are starches that are chemically modified to improve their functionality (BeMiller, 2011; Kaur *et al*., 2012). However, concerns about consumer and environmental safety related to the use of chemicals (Zia-ud-Din *et al.*, 2017), has encouraged the development of 'clean label' starches (Maphalla & Emmambux, 2016) prepared by a novel process that is employing approved food ingredients and additives to modify starch. In this study, such modified starches (maize starch modified with stearic acid or with monoglyceride) were used as fat replacers in mayonnaise-type food emulsions and they were evaluated in terms of rheology, tribology and sensorial properties.

Mayonnaise is a semi-solid, oil-in-water emulsion generally described as a high-fat and high-calorie food (Mun et al., 2009; Lee *et al*., 2013), that traditionally contains 70-80 % fat (Depree & Savage, 2001). The production and quality characteristics of low-calorie mayonnaise emulsions have been studied extensively at different levels of fat reduction, but the challenge of not compromising the desirable sensory properties continues to be critical in the food industry. For instance, the addition of beta-glucan as a fat replacer adversely affected the appearance and colour of reduced-fat mayonnaise resulting in a significantly lower perceived sensory quality in comparison with the full-fat control sample (Worrasinchai *et al*., 2006). Mayonnaise is generally described as being creamy, pale yellow, mild-flavoured and spoonable (Duncan, 2004; Ma & Boye, 2013). These desirable quality attributes must, therefore, be attempted for in reduced-fat mayonnaise for optimum product and consumer acceptability.

Mayonnaise-emulsions with fat replacement levels up to 50 % were formulated with fat mimetics based on whey protein isolate and low-methoxy pectin (Liu *et al*., 2007) and on potato powder mash (El-Bostany *et al*., 2011). In the related research, reduced-fat mayonnaise was formulated by replacing part of the oil with gelatinised rice starch and xanthan gum, and the effect of their inclusion on rheological properties was investigated (Lee *et al.*, 2013). Stable mayonnaise-type emulsions were prepared by replacing up to 30 % fat, which resulted in a 23 % lower energy content in comparison to full-fat mayonnaise while the emulsions exhibited similar rheological properties as a commercial reduced-fat mayonnaise. In the formulation of reduced-calorie emulsion-based sauces and dressings, Chung, Degner and McClements (2014) demonstrated the effectiveness of using microparticulated whey protein in combination with polysaccharides to formulate emulsions with appearance and consistency similar to their full-fat versions.

The amount of oil substituted by a fat replacer is an important quality characteristic of the low-fat mayonnaise produced. Products with oil substitution levels as high as 80 % based on 'clean-label' starches were studied by Teklehaimanot *et al*. (2013); in this research the effects of teff and maize starches modified with 1.5 % stearic acid on the rheological properties, microstructure, freeze-thaw, and high-temperature stability of mayonnaise-type-emulsions were determined. It was found that replacing sunflower oil at 50 % and 80 % levels with stearic acid modified maize starch produced low-calorie mayonnaise type emulsions with higher viscosity and smaller oil droplets compared to full-fat mayonnaise. All the low-calorie mayonnaise type emulsions showed shear-thinning behaviour and were more stable to freeze-thaw cycles and high-temperature storage than full-fat mayonnaise. However, the effect of such substantial oil replacement by maize starch/stearic acid on the sensory profile of the resulting low-calorie mayonnaise type emulsions were not researched. Also, no research was conducted on the tribological properties of these emulsions (i.e. thin layer lubrication) that affect mouthfeel and texture perception during oral processing, while these are not fully determined by bulk rheology.

This study, therefore, investigates the impact of substituting sunflower oil with two lipid-modified maize starch fat-replacers (maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride) on the lubricating properties of the reduced-fat mayonnaise-type emulsions in relation to their mouthfeel textural sensory attributes and rheological properties.

3.2.2 Materials and Method

3.2.2.1 Materials

Potential fat replacers used for the production of the reduced-fat mayonnaise-type emulsions were produced by modifying maize starches with stearic acid and monoglyceride according to the method by D'Silva *et al*., (2011). Commercial white maize starch, stearic acid, glycerol monostearate and Citri-Fi® 100 FG (a commercial citrus-base fat replacer) used in the study are described in the previous chapter. Spray-dried egg yolk was purchased from Sunspray Food Ingredients (Pty) Ltd. (Johannesburg, South Africa). Potassium sorbate and sodium benzoate were purchased from Merck Chemicals (Pty) Ltd. (Midrand, South Africa). All other ingredients (sunflower oil, vinegar (5 % acidity), sugar, salt, and mustard powder) were purchased from a local supermarket.

Two commercial mayonnaise products (Crosse & Blackwell high and low-fat mayonnaise): high-fat (52 % oil) and low-fat (25 % oil) were purchased from a local supermarket and used as references in this study. The commercial high-fat mayonnaise contained thickeners, acidity regulators, colourants and flavourings. The commercial low-fat mayonnaise (25 % oil), in addition to all the above, also contains chemically modified maize starch.

3.2.2.2 Reduced-fat mayonnaise-type-emulsions formulation

Mayonnaise trial formulations were obtained by adjusting the percentage of ingredients from existing literature formulations (Su, Lien, Lee & Ho, 2010; El-Bostany *et al*., 2011; Teklehaimanot *et al*., 2013) after several laboratory trials. Tests were done by first varying the levels of ingredients (sunflower oil, egg yolk, vinegar, salt and sugar) and then keeping them constant to make provision for replacing some percentage of sunflower oil with the freshly produced fat replacers. In the formulation development phase, trial mayonnaise samples (full-fat and low-fat) were informally assessed by sensory scientists of the Department of Consumer and

Food Sciences until the samples were rated acceptable. Compositions of the final experimental samples used in this study are presented on a 100 g oil basis (Table 3.2.1).

3.2.2.3 Preparation of reduced-fat mayonnaise-type emulsions

The method by Teklehaimanot *et al.* (2013) was used with some modifications. The aqueous phase (vinegar, egg yolk, salt, sugar, mustard and preservatives) was homogenized for 1 min at 4500 rpm using a Silverson high shear homogenizer L5T (Silverson Machines Ltd. Waterside, Chesham Bucks. England). Sunflower oil was then added gradually to the mix for 2 min while increasing the homogenizing speed from 4500 rpm to 8000 rpm. The final emulsion was then homogenized at 8000 rpm for 2 min. In the case of the reduced-fat mayonnaise-type emulsions, 10 % (w/w) suspensions of each fat replacer [maize starch with 1.5 % stearic acid and maize starch with 2 % monoglyceride (w/w)] was initially wet heat processed (pasted) using a reactor (IKA® LR 1000 control) at 91 °C at 150 rpm for 30 min and mixed thoroughly with the aqueous phase before adding the oil. The emulsions were then poured into glass bottles and stored at 4 °C for further analysis within two weeks.

3.2.2.4 pH and water activity (a_w) measurements

pH and a_w values were measured at a temperature of 23 – 24 °C using an electronic bench pH meter (Microprocessor pH 211, HANNA® products, Italy) and a water activity meter (AQUALAB Pawkit Water Activity Meter, USA), respectively.

3.2.2.5 Colour measurements

The mayonnaise samples were measured for colour using the L*, a*, b* system using a colour meter (Minolta Chroma meter CR-400/410, Konica Minolta Sensing, Japan), which was calibrated using a white standard porcelain plate (Y =85.7, X = 0.3166, y = 0.3242). In this colour system, L* represents the lightness, whereby +a represents the red coordinate, −a is the green coordinate, +b is the yellow coordinate, and −b is the blue coordinate. The data was also represented in terms of hue angle (H) and chroma (C).

3.2.2.6 Microscopy analysis

Mayonnaise samples were observed under a bright field using a Nikon Optiphot Transmitted Light Microscope (Tokyo, Japan). A drop of the sample was placed on a slide and covered with a coverslip for observation. Microscopic images were taken with the 200x objective.

3.2.2.7 Descriptive sensory evaluation

Ethical approval for this study was obtained from the ethics committee of the Faculty of Natural and Agricultural Sciences, University of Pretoria, South Africa (EC170425-111).

Ten panellists (6 females and 4 males) between the 19 to 52 years constituted the trained descriptive sensory panel (8 of whom were part of the panel that previously assessed the sensory attributes of the starch-lipid complexes used in this study).

Two sessions (2 hours each) were used for the development of descriptors, definitions, agreement on references, and training on the use of scales. Panellists were given a list of potential mayonnaise descriptors (obtained from existing literature and focus group discussion using students from the Department of Consumer and Food Sciences, University of Pretoria) and asked to check attributes that best describe the mayonnaise samples. They were also asked to include additional attributes that might have been omitted. For the development of descriptive terms, the two commercial samples of mayonnaise and four (4) experimental samples were used (Table 3.2.2). Once all samples were evaluated by the panellists, sessions of discussions were held to reach consensus on the list of terms with their definitions. Reference samples were also presented to panellists and consensus reached on anchoring the attributes on 10 point structured scales. A list of mouthfeel attributes, definitions, references and scale used for evaluating the mayonnaise samples is given in Table 3.2.3.

A randomized complete block design was used for the actual product evaluation. Eight (8) experimental samples were used in addition to the two (2) commercial samples (Table 3.2.2). About 2 ml of each sample was presented monadically at a temperature of 4 -6 °C in glass ramekins covered with foil with stainless steel spoons. Samples were coded with a 3-digit number. Panellists were given lukewarm water (40 °C), recommended for products that leave an oily residue (The ASTM E1871 Standard, 2006) and carrots as palate cleansers.

All evaluations were performed by panellists seated in individual evaluation booths with white daylight illumination. The panellists were instructed to evaluate each sample by first lifting the side of the foil covering the ramekins and smelling to assess the sample for aroma attributes followed by appearance attribute. Samples were then placed in the mouth, and the flavour, mouthfeel, and aftertaste attribute assessed. A structured 10-point line scale was used to measure the intensities of the different attributes for each sample. Zero indicated the absence of the attribute being measured, while 10 indicated a high intensity of perception. Panellists evaluated all 10 samples in triplicate over three sessions lasting 2 h per day.

Compusense cloud (Compusense Inc., Guelph, Canada) was used to design the test setup, generate random codes and to capture responses from the trained panel.

3.2.2.8 Tribology measurements (friction coefficient)

Tribology measurements were performed with a Mini-Traction Machine (MTM2. PCS Instruments Ltd. UK), using an elastomeric tribo-pairs PDMS (polydimethylsiloxane) disk and ball, to mimic the soft nature of the oral surfaces of interest, i.e. tongue and palate *(Bongaerts et al.*, 2007). The instrument was coupled with an external water bath keeping the temperature in the measurements chamber at 35 ± 1 °C during the experiments. A load of 2 N was applied in all experiments while sliding-to-roll ratio (SRR), was set to 50 % to mimic the relative movement of the tongue and soft palate in the oral cavity.

For each sample, two tribology experiments were done while using a new PDMS tribo-pair, a ball, and a disk, each time. Mayonnaise samples (15 g) were poured into the mini-traction machine measurement chamber onto the disk. The ball and the disk were brought into a loaded contact and the entrainment speed was ramped from 750 mm/s to 1 mm/s and then back to 750 mm/s, while friction was accessed at 40 logarithmically spaced speeds during each ramp. Three ramping cycles immediately after each other were performed. The results for each speed are presented as an average of six friction coefficient values obtained during the three down-speed and the three up-speed ramps.

3.2.2.9 Flow property measurement

Flow properties were determined, according to Teklehaimanot *et al.* (2013) with modifications. The shear behaviour of the experimental samples was determined with a Physica MCR 101 Rheometer (Anton Paar, Ostfildern, Austria) using a vane and cup method. The shear rate was increased from; 0.01/s to 1000/s and reduced back from 1000/s to 0.01/s at 25° C and data fitted to the Power law equation $\delta = k\dot{\gamma}^n$, where δ is the shear stress measured in Pascal (Pa), and $\dot{\gamma}$ is the shear rate (s^{-1}). K and n are the consistency coefficient (Pas) and the flow behaviour index, respectively. Where n = 1 for a Newtonian fluid, n < 1 for shear thinning and n > 1 for shear thickening materials.

3.2.2.10 Texture measurements

The texture of mayonnaise type emulsions was determined with an EZ-test texture analyzer (EZ–L, Shimadzu Tokyo, Japan). Samples were gently scooped into cylindrical containers (40 mm x 55 mm). Using a 35 mm probe, samples were compressed at a speed of 1 mm/s, to a sample depth of 40 mm, and then retracted. From the resulting force-time curve, the values for texture attributes, i.e. firmness and adhesiveness, were obtained. Firmness was calculated as the maximum force reached before the probe penetrates the sample and adhesiveness as the area below the negative force vs distance curve, representing the work necessary to pull the compressing probe away from the sample.

3.2.2.11 Statistical analysis

A multivariate analysis of variance (MANOVA) was used to determine the effect of the independent variables [oil replacement levels (50, 80, and 98 %) and different potential fat replacers (MS+SA, MS+MG, and a commercial fat replacer)] on the rheological, tribological and textural properties of the mayonnaise-type emulsions and the least significant difference test (LSD) was used to separate the means ($p \leq 0.05$). Statistical analysis was performed using IBM SPSS version 20 (SPSS, Inc., 1998, Chicago, IL). For the sensory ratings, a two way ANOVA without interactions was conducted on the independent variables (samples and panellists) and the LSD test used to separate the means using XLSTAT 2014. Principal component analysis (PCA) was used to show the relationship between tribology, rheology and sensory properties of the different mayonnaise-type emulsions.

Table 3.2.1. Composition (g) of experimental samples

Ingredients	*Full-fat***	*50 % oil replacement*	*80 % oil replacement*	*98 % oil replacement*
Sunflower oil	280	140	56	5.6
Spray dried egg yolk	48	48	48	48
Vinegar	60	60	60	60
Salt	4	4	4	4
Sugar	4	4	4	4
Powdered mustard	1.98	1.98	1.98	1.98
Potassium sorbate	0.12	0.12	0.12	0.12
Sodium benzoate	0.12	0.12	0.12	0.12
*Fat replacers**	na	140	224	274.4

* Maize starch modified with 1. 5 % stearic acid / Maize starch modified with 2 % monoglyceride
****** 70 % oil content

Table 3.2.2. Oil content (%) of reduced-fat mayonnaise-type emulsions and commercial mayonnaise (reference) used in the study

Mayonnaise samples	*Oil content %***
Full-fat (control – no fat replacer)	70
50 % (Maize starch + 1.5 % stearic acid)*	35
80 % (Maize starch + 1.5 % stearic acid)*	14
98 % (Maize starch + 1.5 % stearic acid)*	1.4
50 % (Maize starch + 2 % monoglyceride)*	35
80 % (Maize starch + 2 % monoglyceride)*	14
98 % (Maize starch + 2 % monoglyceride)*	1.4
50 % (Commercial fat replacer mayonnaise)*	35
Commercial high-fat (reference)	52
Commercial low-fat (reference)	25

* Percentage of oil replaced by fat replacer with respect to oil content in the full-fat formulation
** Oil content as a weight fraction of the whole emulsion

Table 3.2.3. Sensory attributes used by panel for evaluation of mayonnaise samples

Attributes	*Definition*	*References (10 on the scale)*	*Scale (from 0 to 10)*
	Flavour & in-mouth texture		
Bitter	Intensity of basic taste of which caffeine in water is typical	4 % w/w Caffeine solution	Not bitter – very bitter
Thick	Force required to compress a sample between the tongue and palate		Not thick – very thick
Smooth	The absence of detectable particles in the sample.	Double-cream yoghurt	Not smooth – very smooth
Creamy	The intensity of creaminess	Double-cream yoghurt	Not creamy – very creamy
Mouth-coating	The extent to which sample forms a coating in the mouth during and after oral processing	Lard fat	Not mouth-coating – very mouth-coating
Melting	How easily the sample melted in the mouth		Melted slowly – melted very fast
Ease-to-swallow	Amount of effort required to swallow	Water	Not easy-to-swallow – very easy-to-swallow

3.2.3 Results

The substitution of sunflower oil in reduced-fat mayonnaise-type emulsions with fat replacers (maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride) showed differences in their sensory characteristics as well as on their tribological, and rheological properties. The sensory and physicochemical characteristics are summarised in Figures 3.2.1-3.2.3 and Tables 3.2.6, 3.2.7, 3.2.8, while the relationship between these quality characteristics is also presented using a PCA biplot in Figure 3.2.4.

3.2.3.1 Water activity, pH, microstructure and colour of reduced-fat mayonnaise type-emulsions

Water activity and pH of all the mayonnaise-type emulsions ranged between 0.97 to 0.99 and 3.84 to 3.85, respectively (Table 3.2.4). The water activity and pH readings for all the reduced-fat mayonnaise-type emulsions were slightly but significantly higher ($p < 0.05$) than those of the full-fat mayonnaise sample with water activity and pH of 0.95 and 3.77 respectively.

The optical microscopy measurements revealed that increasing the levels of fat replacers that is, decreasing oil content, caused a reduction in oil droplet size in the 50 % and 80 % oil replaced reduced-fat mayonnaise-type emulsions (Figure 3.2.1). Oil droplets were evenly distributed within the continuous phase, with very few oil droplets observed within the continuous phase of 98 % fat-replaced samples.

The colour of the reduced-fat mayonnaise-type emulsions is presented in the form of coordinates in CIE L*, a*, b* colour space, and chroma and hue-angle values (Table 3.2.5). When comparing the lightness (L*) of the reduced-fat mayonnaise-type emulsions to the full-fat control, lightness values for the 50 % and 80 % oil replacement are significantly higher ($p < 0.05$) than for the full-fat mayonnaise sample. However, at 98 % oil replacement, the lightness was significantly lower ($p < 0.05$) compared to the full-fat mayonnaise. Similarly, a significant decrease in ‘a*’ values (redness) and increase in ‘b*’ values (yellowness) were observed when 98 % of the oil was replaced for both types of fat-replacers. Also, the chromaticity (C*) and hue (h*) values of the reduced-fat mayonnaise-type emulsions significantly increased ($p < 0.05$) for the samples with 98 % oil replacement in comparison to the full-fat emulsion, while these values were still significantly lower ($p < 0.05$) than for the two commercial mayonnaises samples that contained colorants.

Table 3.2.4. Effect of lipid-modified maize starch fat replacers on the water activity (a_w) and pH of reduced-fat mayonnaise-type emulsions

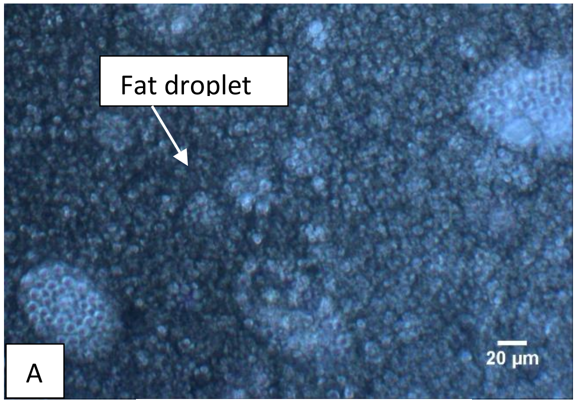
Mayonnaise samples	*Fat replacement (%)*	a_w	*pH*
Full-fat (control, 70 % oil)	na	$0.95^{b} \pm 0.0$	$3.77^{b} \pm 0.0$
Maize starch + 1.5 % stearic acid	50	$0.97^{bc} \pm 0.0$	$3.85^{d} \pm 0.0$
	80	$0.97^{bc} \pm 0.0$	$3.84^{d} \pm 0.0$
	98	$0.99^{c} \pm 0.0$	$3.84^{d} \pm 0.0$
Maize starch + 2 % monoglyceride	50	$0.98^{c} \pm 0.0$	$3.85^{d} \pm 0.0$
	80	$0.97^{bc} \pm 0.0$	$3.84^{d} \pm 0.0$
	98	$0.97^{bc} \pm 0.0$	$3.85^{d} \pm 0.0$
Commercial fat replacer mayonnaise	50	$0.98^{c} \pm 0.0$	$3.82^{c} \pm 0.0$
Commercial high-fat (52 % oil)	na	$0.92^{a} \pm 0.0$	$2.68^{a} \pm 0.0$
Commercial low-fat (25 % oil)	na	$0.95^{b} \pm 0.0$	$2.69^{a} \pm 0.0$

- Values are means of triplicate readings with standard deviation
- Mean values in the same column with different superscripts differ significantly ($p < 0.05$)

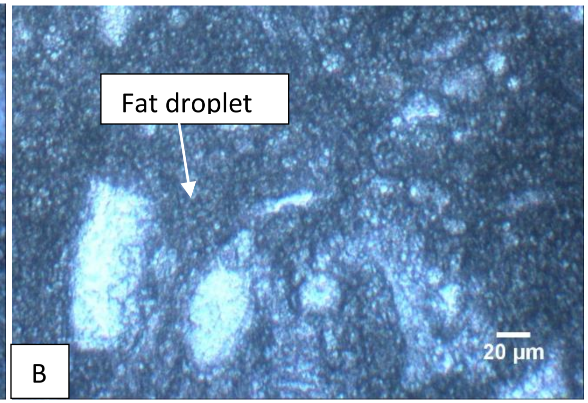
Table 3.2.5. Effect of lipid-modified maize starch fat replacers on the colour parameters of reduced-fat mayonnaise-type emulsions

Mayonnaise samples	*Fat replacement (%)*	*Colour analysis*				
		L*	a*	b*	C*	h*
Full-fat (control, 70 % oil)	na	$82.8^{c} \pm 0.7$	$0.12^{de} \pm 0.3$	$18.5^{cde} \pm 0.5$	$18.5^{cde} \pm 0.5$	$89.6^{abc} \pm 0.9$
Maize starch + 1.5 % stearic acid	50	$86.2^{de} \pm 0.8$	$0.54^{e} \pm 0.3$	$17.8^{cd} \pm 1.3$	$17.8^{cd} \pm 1.3$	$88.3^{a} \pm 0.9$
	80	$84.5^{d} \pm 0.1$	$-0.12^{bcd} \pm 0.2$	$18.0^{cd} \pm 0.2$	$18.0^{cd} \pm 0.2$	$90.4^{bcd} \pm 0.5$
	98	$76.8^{a} \pm 1.4$	$-0.66^{b} \pm 0.1$	$19.8^{ef} \pm 0.5$	$19.8^{e} \pm 0.5$	$91.9^{d} \pm 0.2$
Maize starch + 2 % monoglyceride	50	$86.0^{de} \pm 0.3$	$0.02^{cde} \pm 0.0$	$16.3^{ab} \pm 0.1$	$16.3^{ab} \pm 0.1$	$89.9^{abc} \pm 0.2$
	80	$84.8^{d} \pm 0.3$	$0.20^{de} \pm 0.2$	$17.5^{bc} \pm 0.3$	$17.50^{c} \pm 0.3$	$89.3^{ab} \pm 0.6$
	98	$78.9^{b} \pm 0.5$	$-0.50^{bc} \pm 0.3$	$19.2^{de} \pm 0.3$	$19.2^{de} \pm 0.3$	$91.5^{cd} \pm 0.9$
Commercial fat-replacer mayonnaise	50	$85.9^{de} \pm 0.0$	$0.02^{cde} \pm 0.0$	$15.5^{a} \pm 0.1$	$15.5^{a} \pm 0.1$	$89.9^{a} \pm 0.1$
Commercial high-fat (52 % oil)	na	$85.5^{d} \pm 0.4$	$-4.34^{a} \pm 0.2$	$26.1^{g} \pm 0.3$	$26.5^{g} \pm 0.3$	$99.5^{e} \pm 0.6$
Commercial low-fat (25 % oil)	na	$87.4^{e} \pm 0.2$	$-3.86^{a} \pm 0.2$	$21.0^{f} \pm 0.4$	$21.4^{f} \pm 0.4$	$100.4^{e} \pm 0.8$

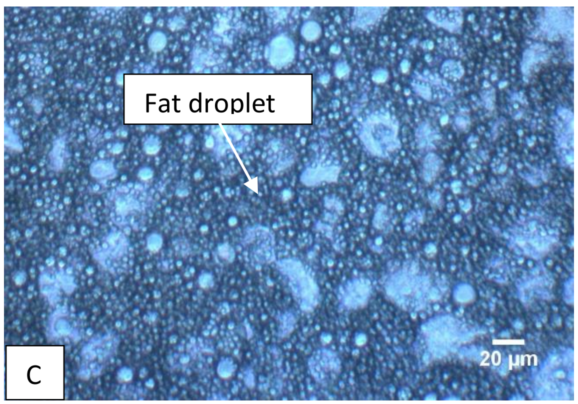
- Values are means of triplicate readings with standard deviation
- Mean values in the same column with different superscripts differ significantly ($p < 0.05$)



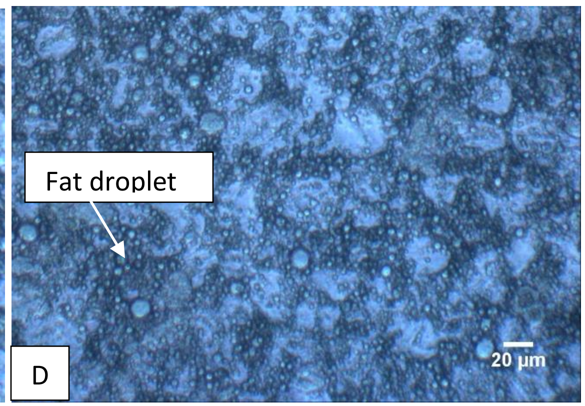
Full-fat (control)



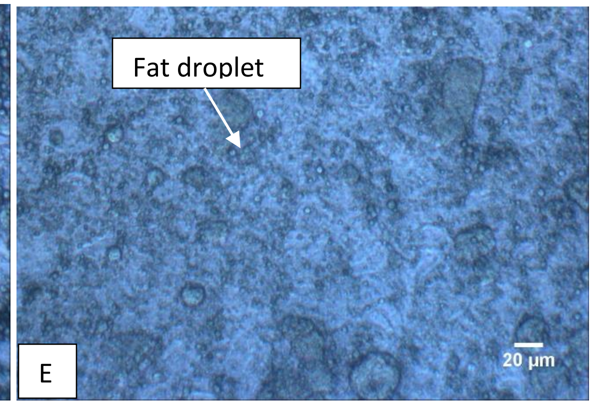
Commercial fat replacer mayonnaise (50 %)



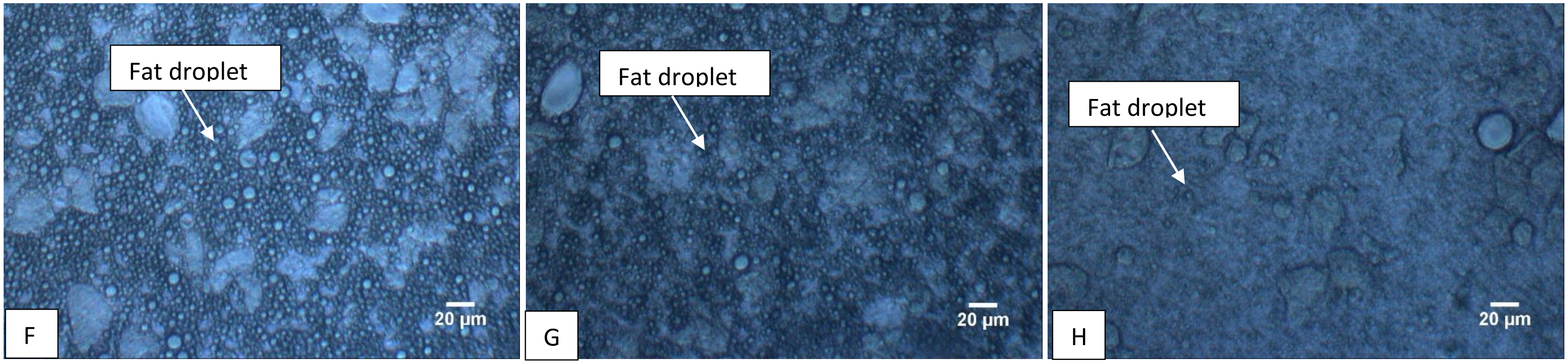
50 % (maize starch + 1.5 % stearic acid)



80 % (maize starch + 1.5 % stearic acid)



98 % (maize starch + 1.5 % stearic acid)



50 % (maize starch + 2 % monoglyceride) 80 % (maize starch + 2 % monoglyceride) 98 % (maize starch + 2 % monoglyceride)

Figure 3.2.1. Effect of lipid-modified maize starch fat replacers on the microstructure of reduced-fat mayonnaise-type emulsions

3.2.3.2 Mouthfeel textural characteristics of reduced-fat mayonnaise-type emulsions

Mean scores of the mouthfeel textural attributes are shown in Table 3.2.6. Eighteen different attributes were evaluated, but only the in-mouth textural sensory attributes were tested for correlation to tribology and rheology in the PCA analysis are discussed.

Panellist rated oiliness (fattiness) of all the reduced-fat mayonnaise-type emulsions significantly lower ($p < 0.05$) compared to the full-fat mayonnaise control (Table 3.2.6). For the reduced-fat mayonnaise-type emulsions, there is a trend, although not significant, for a reduction in the perceived oiliness with the increasing level of fat-replacement.

The thickness of the reduced-fat mayonnaise-type emulsion containing starch/stearic acid was significantly lower ($p < 0.05$) compared to the mayonnaise formulated with starch/monoglyceride and the full-fat mayonnaise (Table 3.2.6). Oil replacement level (50, 80 and 98 %) did not affect ($p > 0.05$) the thickness of emulsions containing starch/stearic acid. For the starch/monoglyceride fat-replacer, the level of fat replacement affected the thickness of emulsions; the perceived thickness of 50 % fat-replaced sample was similar to that of the full-fat emulsion, while the thickness of 80 % and 98 % fat-replaced samples was significantly higher ($p < 0.05$) (Table 3.2.6).

Panellist rated all the reduced-fat mayonnaise-type emulsions high for smoothness, melting, and easy-to-swallow. The different fat replacers and oil replacement levels did not significantly affect ($p > 0.05$) the smoothness, melting, and ability to swallow. On the other hand, choice of fat-replacer significantly affected ratings for the creaminess and mouth-coating attributes; the emulsions formulated with starch/monoglyceride were statistically similar to that of the full-fat mayonnaise samples, but emulsions formulated with starch/stearic acid were rated significantly less creamy and mouth-coating than the full-fat reference (Table 3.2.6). For both fat-replacers, mean scores for creaminess indicated decrease with the increasing level of fat replacements; however, this trend was not statistically significant.

There is also an interesting trend in astringency ratings, where the mean scores are increasing above those obtained for the full-fat sample with the increasing level of fat replacement. The significant difference in comparison to the full-fat reference was reached at 98 % fat replacement level by starch/stearic acid and for 80 % and 98 % fat replacement level for starch/monoglyceride. The perception of astringency might be possibly related to the sensory attribute "artificial" that shows a similar trend.

Table 3.2.6. Mean ratings for flavour and texture (in-mouth feel) of reduced-fat mayonnaise-type emulsions

	Full-Fat (control, 70 % oil)	*Decreasing oil concentration* → **Maize starch + 1.5 % stearic acid**			*Decreasing oil concentration* → **Maize starch + 2 % monoglyceride**			*p- value*
		50 %	**80 %**	**98 %**	**50 %**	**80 %**	**98 %**	
Overall-flavour	8.3^{a} ± 1.9	7.6^{ab} ± 2.5	7.1^{b} ± 2.7	6.7^{b} ± 2.8	7.5^{ab} ± 2.8	8.1^{a} ± 2.0	8.2^{a} ± 2.2	0.00
Saltiness	6.3^{a} ± 2.9	4.9^{b} ± 3.1	4.8^{b} ± 3.6	4.8^{b} ± 3.1	5.3^{ab} ± 3.3	5.2^{b} ± 3.3	4.8^{b} ± 3.0	0.05
Thickness	3.4^{b} ± 3.0	1.1^{c} ± 1.8	1.2^{c} ± 2.0	0.5^{c} ± 1.0	4.3^{b} ± 2.6	5.7^{a} ± 3.0	5.7^{a} ± 3.4	0.00
Smoothness	8.9^{a} ± 2.0	8.4^{ab} ± 2.7	8.3^{b} ± 2.6	8.3^{b} ± 2.6	8.5^{ab} ± 2.1	8.8^{ab} ± 1.9	8.7^{ab} ± 1.9	0.13
Bitterness	3.1^{bc} ± 3.7	2.5^{c} ± 3.1	2.9^{bc} ± 3.1	3.8^{ab} ± 3.7	2.9^{bc} ± 2.9	3.2^{abc} ± 3.1	4.3^{a} ± 3.8	0.06
Starchy	2.9^{a} ± 3.3	2.3^{a} ± 2.8	3.2^{a} ± 3.3	2.6^{a} ± 3.4	2.9^{a} ± 3.0	3.3^{a} ± 3.5	3.6^{a} ± 3.6	0.52
Eggy	4.8^{a} ± 2.9	4.5^{a} ± 2.7	4.4^{a} ± 2.6	4.8^{a} ± 3.6	4.5^{a} ± 2.7	4.6^{a} ± 2.7	4.5^{a} ± 2.7	0.99
Oiliness	6.9^{a} ± 2.8	4.4^{bc} ± 3.4	4.3^{bc} ± 3.0	3.7^{c} ± 2.8	5.2^{b} ± 2.8	5.1^{b} ± 3.2	4.9^{b} ± 3.3	0.00
Vinegar flavour	6.5^{a} ± 3.0	5.9^{a} ± 2.8	6.0^{a} ± 2.4	6.4^{a} ± 2.7	6.2^{a} ± 2.3	7.1^{a} ± 2.3	6.9^{a} ± 2.1	0.42
Creaminess	7.3^{a} ± 2.7	6.2^{bc} ± 3.4	5.2^{cd} ± 3.9	5.0^{d} ± 4.0	7.3^{a} ± 2.7	7.1^{ab} ± 2.9	6.7^{ab} ± 3.3	0.00
Sweet	2.7^{a} ± 3.1	2.1^{ab} ± 2.0	1.9^{abc} ± 2.2	1.5^{bc} ± 2.0	2.2^{ab} ± 2.5	1.5^{bc} ± 1.7	1.2^{c} ± 1.6	0.01
Mustard	3.2^{a} ± 3.4	3.1^{a} ± 2.4	3.4^{a} ± 2.9	3.5^{a} ± 3.2	3.0^{a} ± 2.4	3.4^{a} ± 2.8	4.1^{a} ± 3.4	0.66
Mouth-coating	4.4^{a} ± 3.0	2.6^{b} ± 2.9	3.0^{b} ± 3.2	2.8^{b} ± 3.1	3.6^{ab} ± 3.4	3.7^{ab} ± 3.5	4.3^{a} ± 3.5	0.00
Melting	8.7^{bc} ± 1.8	9.2^{ab} ± 1.3	9.3^{a} ± 1.2	9.4^{a} ± 0.8	8.5^{c} ± 1.9	8.7^{bc} ± 1.8	8.1^{c} ± 2.4	0.00
Ease-to-swallow	9.1^{a} ± 1.3	9.2^{a} ± 1.2	9.0^{ab} ± 1.6	9.0^{ab} ± 1.9	9.0^{ab} ± 1.4	8.8^{bc} ± 1.6	8.5^{c} ± 1.8	0.00
Astringent	3.4^{b} ± 3.0	3.7^{b} ± 3.1	4.5^{ab} ± 3.4	5.2^{a} ± 4.1	4.6^{ab} ± 3.8	5.4^{a} ± 3.9	5.6^{a} ± 4.0	0.00
Artificial	2.2^{d} ± 3.1	2.7^{cd} ± 3.0	3.3^{bc} ± 3.6	3.9^{ab} ± 4.3	2.9^{bcd} ± 3.4	3.6^{bc} ± 3.6	4.7^{a} ± 4.0	0.00
Tangy	6.2^{abc} ± 3.3	5.9^{abc} ± 3.1	5.8^{bc} ± 3.4	4.8^{c} ± 3.7	5.8^{bc} ± 3.1	6.6^{ab} ± 3.4	7.3^{a} ± 2.6	0.04

- Values are means of panel ratings
- Mean values in the same row with different superscripts differ significantly ($p < 0.05$)

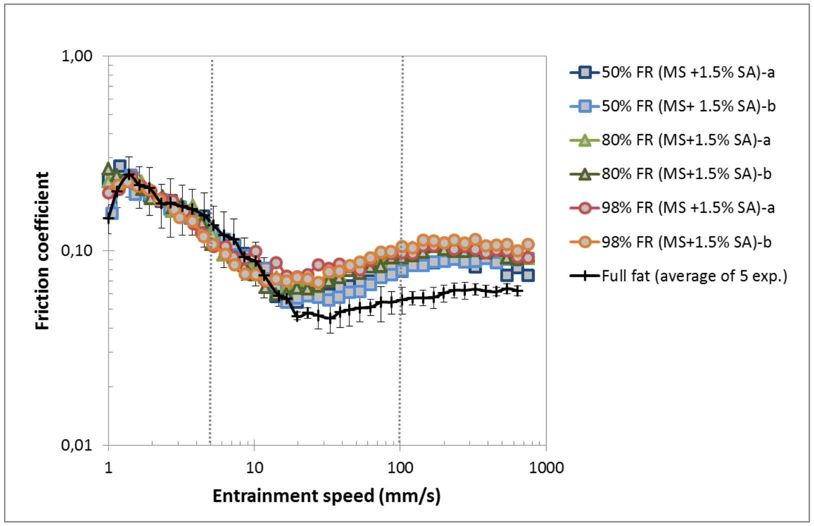
3.2.3.3 Tribology of reduced-fat mayonnaise-type emulsions

The Stribeck curves of all samples were relatively similar. They feature mixed lubrication regime up to entrainment speed of about 15-20 mm/s, characterised by friction coefficient decreasing with speed, followed by full elastohydrodynamic regime (EHL), characterised by the increase of friction coefficient with the entrainment speeds. A distinctive additional feature of the Stribeck curves of all reduced-fat mayonnaise-type emulsions containing fat-replacers (Figure 3.2.2 a, b) is the presence of “hump” at (high) entrainment speeds of about 200 mm/s, while the corresponding feature is absent for the full-fat reference with no fat-replacer.

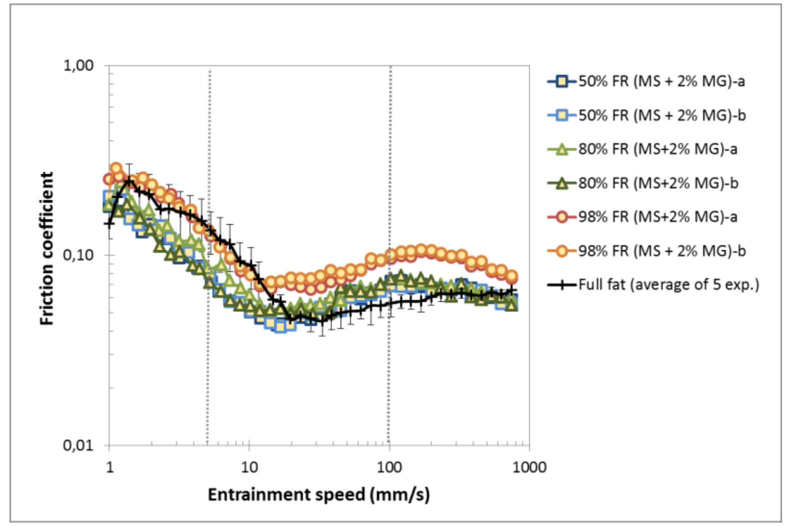
In the mixed regime, the surfaces are in partial contact and friction is affected both by lubricant fluids that are partly entrained between surfaces and by interfacial phenomena such as surface roughness, surface chemistry and adsorption of the components of lubricant fluid onto surfaces. In the elastohydrodynamic lubrication regime, the surfaces are fully separated by a lubricant film, and the friction is determined by the bulk properties of lubricant fluids.

Friction coefficient values obtained for the mayonnaise emulsions in the mixed regime, at the speed of 5 mm/s, and in the elastohydrodynamic regime, at the speed of 100 mm/s, are presented in Table 3.2.7. In the mixed regime, the friction coefficient values measured for the reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid fat replacers were not significantly different ($p > 0.05$) from those for the full-fat sample, however, significantly lower friction was measured for the reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride at 50 % and 80 % fat replacer levels. In the elastohydrodynamic regime, it was, on the other hand that the starch/monoglyceride emulsions with lower friction were similar to the full-fat emulsion, while the friction coefficient values for the starch/stearic acid emulsions were significantly higher ($p < 0.05$) than for full-fat sample in this regime. Only at the highest level of fat substitution, 98 %, by starch/monoglyceride, the friction in the elastohydrodynamic regime became higher than for the full-fat sample and similar to that measured for the starch/stearic acid emulsions. The choice of lipid used to modify maize starch as the fat replacer apparently affected lubrication properties of the reduced-fat emulsions. In both mixed and elastohydrodynamic lubrication regimes, the reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid showed rise to higher friction (i.e. were less lubricious) than the corresponding emulsions formulated with starch/monoglyceride.

In general, all reduced-fat mayonnaise-type emulsions exhibited good lubrication and the tribological differences to the full-fat reference were relatively small.



(a)



(b)

Figure 3.2.2a, b Effect of lipid-modified maize starch fat replacers on the friction coefficient of reduced-fat mayonnaise-type emulsions containing different levels (50, 80 & 98%) of maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride

- MS – Maize starch, SA - Stearic acid, MG – Monoglyceride

Table 3.2.7. Friction coefficient of the different reduced-fat mayonnaise-type emulsions at sliding speeds 5 mm/s (mixed lubrication regime) and 100 mm/s (hydrodynamic regime)

Mayonnaise samples	*Fat replacement (%)*	*Friction coefficient (μ) 5 mm/s*	*Friction coefficient (μ) 100 mm/s*
Full-fat (control, 70 % oil)	Na	$0.14^{a} \pm 0.03$	$0.06^{c} \pm 0.01$
Maize starch + 1.5 % stearic acid	50	$0.12^{a} \pm .00$	$0.08^{b} \pm 0.00$
	80	$0.12^{a} \pm 0.01$	$0.10^{a} \pm 0.01$
	98	$0.11^{ab} \pm 0.00$	$0.10^{a} \pm 0.01$
Maize starch + 2 % monoglyceride	50	$0.08^{b} \pm 0.01$	$0.07^{bc} \pm 0.00$
	80	$0.08^{b} \pm 0.01$	$0.08^{bc} \pm 0.00$
	98	$0.13^{a} \pm 0.01$	$0.10^{a} \pm 0.00$

- Values are means of replicate readings with standard deviation
- Mean values in the same column with different superscripts differ significantly ($p < 0.05$)

3.2.3.4 Flow properties of reduced-fat mayonnaise-type emulsions

All the emulsions exhibited shear thinning behaviour ($n < 1$, from Power law model) with their flow behaviour index, n, ranging from 0.18 to 0.39 (Table 3.2.8). Oil replacement significantly and progressively decreased ($p < 0.05$) the n-values. Reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride had lower n-values compared to the option formulated with starch/stearic acid.

Addition of the modified starches increased the hysteresis area of the reduced-fat emulsions compared with the full-fat mayonnaise. Reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride fat replacer had significantly higher ($p < 0.05$) hysteresis values compared to the emulsions formulated with starch/stearic acid fat replacer (Table 3.2.8).

The plot of viscosity versus shear rate of the reduced-fat mayonnaise-type emulsions at different levels of oil replacement (Figure 3.2.3), shows that the emulsions prepared using starch/monoglyceride had significantly higher ($p < 0.05$) zero-shear viscosities compared with reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid as fat replacer. Nonetheless, the consistency coefficient, K values obtained for all the reduced-fat mayonnaise-type emulsions formulated using the fat-replacers were significantly lower ($p < 0.05$) compared to the full-fat mayonnaise and the commercial high-fat and low-fat mayonnaise references (Table 3.2.8). Reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid fat replacer had the lowest consistency coefficient values, while the mayonnaise formulated with the commercial fat replacer, on the other hand, recorded the highest consistency coefficient. Firmness and adhesiveness of the reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride fat replacers were significantly higher ($p < 0.05$) than for their counterparts formulated with starch/stearic acid fat replacers and for the full-fat emulsion.

Mayonnaise formulated by replacing 50 % of sunflower oil with the commercial fat replacer was substantially different from the other reduced-fat mayonnaise-type emulsions. It had significantly ($p < 0.05$) the highest consistency coefficient, hysteresis, zero-shear viscosity, firmness and adhesiveness compared to all the experimental samples.

Table 3.2.8. Effect of lipid-modified maize starch fat replacers on the flow – properties [consistency coefficient (K) and flow behaviour index (n) determined from the power law model, hysteresis and zero shear viscosity] and textural properties [firmness and adhesiveness] of reduced-fat mayonnaise-type emulsions

Mayonnaise samples	*Fat replacement (%)*	*n*	*K (Pa s^n)*	*Hysteresis (Pa s)*	*Zero shear viscosity (Pa.s)*	*Firmness (N)*	*Adhesiveness (N)*
Full-fat (control, 70 % oil)	na	0.30^{de} ± 0.0	48.1^{c} ± 2.0	20201^{a} ± 4804	3146.7^{d} ± 85	0.16^{b} ± 0.01	-0.04^{d} ± 0.01
Maize starch + 1.5 % stearic acid	50	0.39^{g} ± 0.0	11.7^{a} ± 0.2	23524^{ab} ± 1521	510.3^{a} ± 32	0.11^{a} ± 0.00	-0.03^{d} ± 0.00
	80	0.29^{cd} ± 0.0	16.8^{a} ± 0.7	25991^{abcd} ± 793	1193.0^{b} ± 25	0.21^{cd} ± 0.02	- 0.05^{d} ± 0.00
	98	0.24^{b} ± 0.0	23.2^{ab} ± 0.7	24471^{abc} ± 1682	660.0^{ab} ± 15	0.17^{b} ± 0.01	-0.04^{d} ± 0.01
Maize starch + 2 % monoglyceride	50	0.31^{d} ± 0.0	22.0^{ab} ± 3.2	35213^{d} ± 1246	3070.0^{d} ± 115	0.19^{bc} ± 0.00	-0.06^{d} ± 0.01
	80	0.20^{a} ± 0.0	35.3^{bc} ± 1.6	34520^{cd} ± 983	3143.3^{d} ± 55	0.27^{ef} ± 0.01	- 0.11^{c} ± 0.03
	98	0.18^{a} ± 0.0	43.4^{c} ± 3.2	31120^{bcd} ± 528	3926.7^{e} ± 135	0.28^{f} ± 0.01	- 0.13^{ab} ± 0.03
Commercial fat replacer mayo	50	0.26^{bc} ± 0.0	90.8^{e} ± 2.0	79225^{f} ± 10320	5253.3^{f} ± 525	0.38^{h} ± 0.01	-0.17^{a} ± 0.02
Commercial high-fat (52 % oil)	na	0.35^{f} ± 0.0	80.5^{e} ± 2.3	47672^{e} ± 2107	3190.0^{d} ± 176	0.34^{g} ± 0.00	-0.13^{ab} ± 0.01
Commercial low-fat (25 % oil)	na	0.32^{e} ± 0.0	65.8^{d} ± 1.2	28788^{abcd} ± 1970	1880.0^{c} ± 36	0.24^{cd} ± 0.01	-0.06^{d} ± 0.00

- Values are means of triplicate readings with standard deviation
- Mean values in the same column with different superscripts differ significantly ($p < 0.05$)
- n and K values were calculated using the upward curve i.e. increasing shear rate from 0.1 to 800 s^{-1} and was calculated from the Power Law model

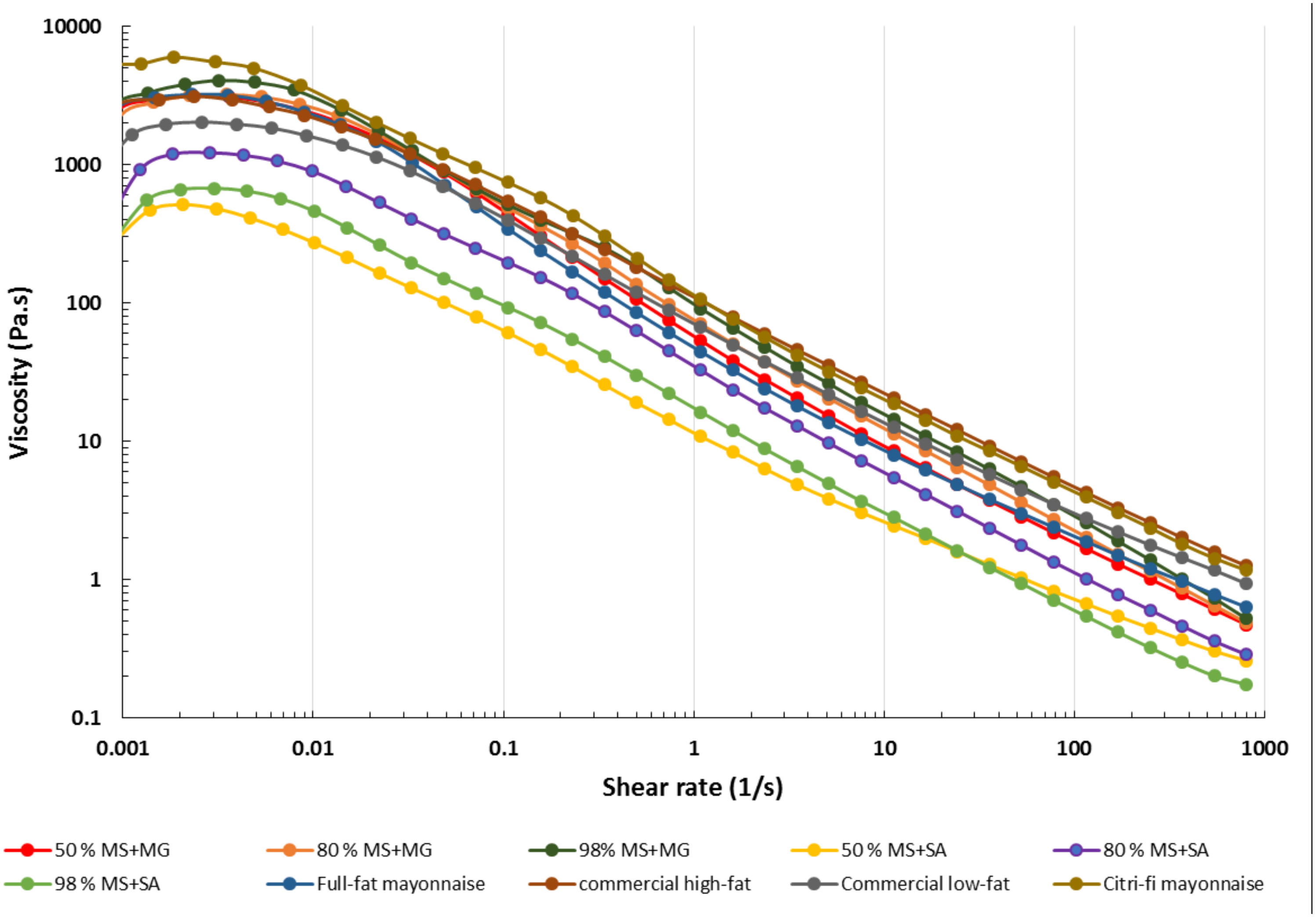


Figure 3.2.3. Effect of lipid-modified maize starch fat replacers on the viscosity of reduced-fat mayonnaise-type emulsions compared with commercial mayonnaise samples

3.2.4 Discussion

The optical properties of the emulsions can be related to the microstructure of the emulsions (Figure 3.2.3). The appearance of an emulsion depends on how transmitted light is either absorbed by chromophores or scattered by oil droplets as the wave propagates through the emulsion (McClements, 2002). Decreasing oil content along with increasing the amount of the different fat replacers decreased the droplet diameters, with droplets more evenly distributed in the continuous phase in comparison to the full-fat mayonnaise. The reduction in the size of droplets made the droplets more available to scatter light in all directions. Also, light scattering is possibly promoted by the presence of semi-crystalline amylose-lipid complexes (Maphalla & Emmambux, 2016). Acosta, Jiménez, Cháfer, González-Martínez and Chiralt (2015) and Thakur, Pristijono, Golding, Stathopoulos, Scarlett, Bowyer, Singh and Vuong (2017) in their study suggested that the presence of crystalline starch increased the number of hydrogen bonds in the continuous phase, which leads to changes in the refractive index of the emulsions. Incorporation of fatty acids into starch-based edible films lowered transparency and increased the light dispersion by the films (Acosta *et al.*, 2015; Thakur *et al.*, 2017). Emulsion opacity can be increased by incorporating non-fat ingredients that exist as particles to effectively scatter light (McClements & Demetriades, 1998).

PCA was applied to correlate tribological and rheological data with in-mouth sensory attributes (Figure 3.2.4), and Pearson's correlation coefficients from PCA were used to evaluate the significance of the relationships between the data (Table 3.2.9). The PCA biplot explained 81.40 % of the variation between the data. The first component (PC1) explained 55.13 % of the total variance, and the second (PC2) accounted for the remaining 26.26 %. PC1 associated reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride with the full-fat mayonnaise and these were separated from the emulsions formulated with starch/stearic acid. The reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride were associated with the following attributes: creaminess, smoothness, mouth-coating, zero-shear viscosity, thickness, firmness, tanginess and astringency. The reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid were, on the other hand, associated with melting and easy-to-swallow attributes.

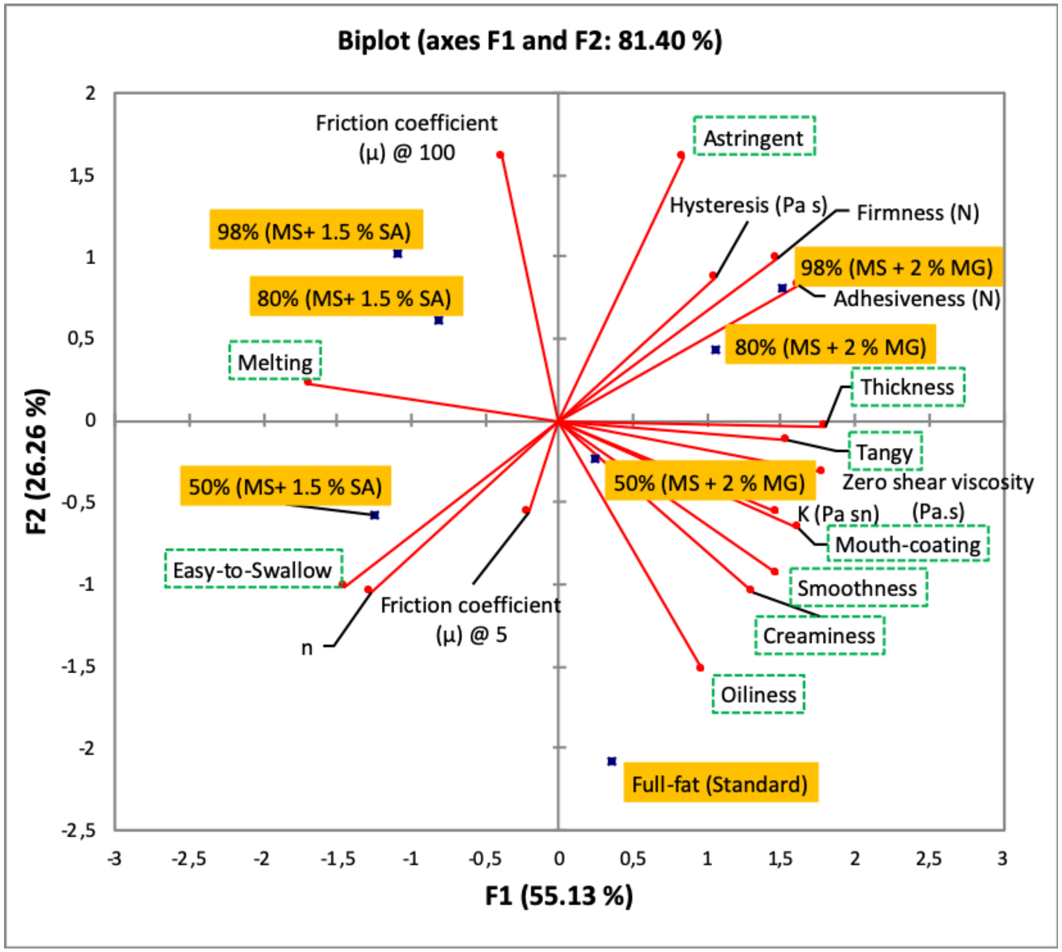


Figure 3.2.4. PCA biplot showing the relationship between tribology, rheology and in-mouth sensory properties ( ) of the different reduced-fat mayonnaise-type emulsions

- MS – Maize starch, SA - Stearic acid, MG – Monoglyceride

Table 3.2.9. Pearson correlation coefficients between tribology, rheology and in-mouth sensory properties of reduced-fat mayonnaise-type emulsions

	Texture & flow properties						*Tribology*		*Sensorial texture (in mouth)*								
Variables	**Firmness (N)**	**Adhesiveness (N)**	**Zero shear viscosity (Pa.s)**	**n**	**K (Pa sn)**	**Hysteresis (Pa s)**	**Friction coefficient (μ) @ 5**	**Friction coefficient (μ) @ 100**	**Thickness**	**Smoothness**	**Oiliness**	**Creaminess**	**Mouth-coating**	**Melting**	**Ease-to-Swallow**	**Astringent**	**Tangy**
Firmness (N)																	
Adhesiveness (N)	**-0.93**																
Zero shear viscosity (Pa.s)	0.68	-0.74															
n	**-0.89**	**0.82**	-0.55														
K (Pa sn)	0.50	-0.54	**0.81**	-0.60													
Hysteresis (Pa s)	0.68	-0.69	0.52	-0.46	0.02												
Friction coefficient (μ) @ 5	-0.26	0.17	-0.11	0.15	0.27	**-0.76**											
Friction coefficient (μ) @ 100	0.29	-0.21	-0.35	-0.41	-0.28	0.03	0.17										
Thickness	0.75	**-0.85**	**0.94**	-0.58	0.68	0.69	-0.28	-0.31									
Smoothness	0.39	-0.49	**0.82**	-0.36	**0.89**	0.13	0.09	-0.62	**0.77**								
Oiliness	0.02	-0.06	0.66	0.05	0.72	-0.13	0.18	**-0.82**	0.50	**0.85**							
Creaminess	0.22	-0.37	**0.80**	-0.05	0.57	0.39	-0.20	**-0.79**	**0.80**	**0.82**	**0.80**						
Mouth-coating	0.53	-0.57	**0.94**	-0.49	**0.93**	0.20	0.16	-0.39	**0.80**	**0.88**	**0.80**	0.73					
Melting	-0.60	0.75	**-0.94**	0.46	-0.68	-0.55	0.03	0.26	**-0.92**	-0.70	-0.53	**-0.78**	**-0.85**				
Ease-to-Swallow	**-0.91**	**0.95**	-0.66	**0.88**	-0.53	-0.57	0.02	-0.43	-0.71	-0.35	0.05	-0.18	-0.54	0.70			
Astringent	**0.80**	**-0.76**	0.29	**-0.85**	0.14	0.68	-0.40	0.63	0.42	-0.05	-0.48	-0.16	0.09	-0.30	**-0.82**		
Tangy	0.65	**-0.80**	**0.77**	-0.42	0.61	0.38	0.20	-0.15	**0.82**	0.69	0.44	0.61	0.71	**-0.82**	-0.70	0.23	

- Values indicate correlation coefficients significant at ($p < 0.05$).
- Green showing high positive correlation and red showing high negative correlation

Oiliness and creaminess ratings (Table 3.2.6) by the sensory panel can be related to the tribology results (Figure 3.2.2a and 3.2.2b) in the elastohydrodynamic regime, where higher oiliness and creaminess was perceived for samples with lower friction coefficient. The reduced-fat emulsions prepared with starch/stearic acid were rated less oily and creamy than the corresponding emulsions prepared with starch/monoglyceride and full-fat emulsion. The PCA biplot (Figure 3.2.4) and Pearson correlation coefficient matrix (Table 3.2.9) showed that the friction coefficient in the elastohydrodynamic regime correlated negatively with oily mouthfeel (-0.82) and creaminess (-0.79), while a weaker negative correlation was also found for smoothness (-0.62). Similar correlations of the measured friction with the perceptions of oiliness and creaminess were found by Dresselhuis, De Hoog, Stuart and Van Aken (2008) that suggested that both tribology and sensory results originated in the different tendencies of the studied emulsions to coalesce. No significant correlation was found for sensory attributes and friction in mixed regime (assessed at 5 mm/s).

All samples showed good lubrication in simulated condition modelled by soft surfaces with high surface roughness. The differences in the tribological properties for different samples were relatively small but still significant. Low friction and similarity of all collected Stribeck curves (Figure 3.2.2a and 3.2.2b) are consistent with a view that contact areas were lubricated by the oil phase for all tested emulsions. The oil that is initially present in the form of emulsified droplets, forms a thin film in the contact area after surface-induced droplet coalescence takes place at the polydimethylsiloxane surfaces. This phenomenon was previously observed in a similar set up by Dresselhuis, Klok, Stuart, de Vries, van Aken and de Hoog (2007), where such coalescence occurred for emulsions with as low as 1 % oil content. Since the lowest oil content in the test samples is 1.4 % (for samples with 98 % level of fat replacement), the presence of oil in the contact area is a reasonable assumption. This assumption is further supported by the presence of the “hump” in the curves collected for the reduced-fat mayonnaise-type emulsions. At entrainment speeds of about 200 mm/s, i.e. well within the full film (elastohydrodynamic) regime, the friction coefficient starts to decrease with speed, which is rather peculiar for full film lubrication during the measurement. Assuming the presence of oil film in the contact area, the “hump” observation could be explained within the contact starvation theory that is well accepted in the field of emulsion-based machine lubricants (Wilson, Sakaguchi & Schmid, 1993). For metal rolling contacts, it was shown that oil is preferentially entrained into contact area at low speeds; however, some water gets entrained along with the oil after reaching critical (high enough) entrainment speed. The presence of water in the contact area then leads to decrease of full film thickness and decrease in friction coefficient for emulsions in comparison to neat oil lubricants (Yang, Schmid, Kasun & Reich, 2004). The phenomena should be more pronounced for emulsions with lower oil content, which is consistent with data obtained in this research when it is present only for the fat-replaced samples with oil content 35 % and lower and absent for full-fat emulsion with 70 % oil.

Possible differences in lubrication behaviour of reduced-fat emulsions formulated with starch/stearic acid and reduced-fat emulsion with starch/monoglyceride may arise from differences in their stability, i.e. in the ability of emulsions components to promote or prevent oil droplet coalescence. It can be hypothesised that the higher friction, which was observed for all reduced-fat emulsions with starch/stearic acid and for 98 % reduced-fat starch/monoglyceride sample, is related to an incomplete/patchy coverage of the polydimethylsiloxane substrates by oil films due to higher stability of oil droplets in the corresponding emulsion matrixes. In the study of Dresselhuis *et al.* (2008) on the relation of in-mouth coalescence of emulsions to the perception of fat, it was shown that the emulsions that were more sensitive to coalescence gave rise to lower friction. In this context, the friction results indicate that fat-reduction by modified starch with amylose-stearic acid complexes lead to more efficient stabilisation of the remaining oil-droplets against coalescence than fat-reduction by modified starch with amylose-monoglyceride complexes; the latter gives rise to higher friction only at the highest fat-replacement level tested. In future, studies of oil droplet stabilisation by resistant starch particles containing amylose-lipid complexes could elucidate the mechanism behind the detected differences between starch/stearic and starch/monoglyceride samples.

The high descriptive sensory ratings for thickness, smoothness, melting and easy-to-swallow for all the reduced-fat mayonnaise-type emulsions can be explained by the rheological properties of the fat replacer containing amylose-lipid complexes that can associate into regular crystalline structures and occur as nanoparticles of less than 100 nm (Zabar *et al*., 2009; Cuthbert *et al*., 2017). These sensory attributes are highly cross-correlated, for example, the perceived thickness of samples was positively correlated to smoothness (0.77), creaminess (0.80), mouth-coating (0.80) and negatively correlated with melting (-0.92) (Figure 3.2.4 and Table 3.2.9). Elmore, Heymann, Johnson and Hewett (1999), Akhtar, Stenzel, Murray and Dickinson (2005), and Chen and Stokes (2012) also observed similar research outcomes. They reported the relationship between creaminess and the amount of fat present in a product in association with attributes like viscosity, taste, aroma, smoothness, and thickness.

Rheological and textural properties play a prominent role in sensory perception. Zero shear viscosity, which was positively cross-correlated with consistency coefficient K, shows significantly high correlation with sensory attributes such as thickness (0.94), smoothness (0.82), creaminess (0.80), and mouth-coating (0.94). Zero shear viscosity, on the other hand, correlated highly negative with the rate of melting (-0.94). The textural property of firmness, which was negatively cross-correlated with adhesiveness, possibly affected sensory perception of thickness (0.75), while a significant negative correlation was found with easy to swallow attribute (-0.91) and positive correlation with perception of astringency (0.80).

Higher thickness ratings for the reduced-fat mayonnaise-type emulsions formulated with starch/monoglyceride can be supported by the high zero shear viscosity and firmness values measured instrumentally (Table 3.2.8). The high zero-shear viscosity and firmness values recorded for the mayonnaise with 50 % commercial fat replacer could be explained by the high concentration of polymers. This possibly caused an increase in molecular entanglement in the commercial fat replacer. Concentrated polymer solutions with constant entanglement density show an increasing zero shear viscosity with increasing concentration (Rao, 2007). Lower firmness of the reduced-fat mayonnaise-type emulsions formulated with the modified starches used in the study compared with the mayonnaise formulated with the commercial fat replacer (Table 3.2.8) can be attributed to the reduced rate of retrogradation due to the presence of the amylose-lipid complexes in the fat replacers (D'Silva *et al.*, 2011).

The zero shear viscosity is substantially affected by the structure and association properties of the amylose-lipid complexes present in the fat-replacers. The viscosity of shear-thinning fluids as shear rate approaches zero, is referred to as it is zero shear viscosity (Rao, 2007; Sunthar, 2010), and indicates its physical stability. The zero shear viscosity phenomenon occurs when a constant density of entanglements is reached between releasing entanglements caused by shearing and their reformation caused by Brownian motions at low shear rates (Rao, 2007; Saha & Bhattacharya, 2010). The higher zero shear viscosity and firmness values imply that reduced-fat emulsions formulated using starch/monoglyceride are more stable at a set position just before shear is applied. Teklehaimanot *et al.* (2013) produced low-calorie reduced-fat mayonnaise-type emulsions with lipid-modified starches that had a lower consistency coefficient, K, (cross-correlated with zero shear viscosity) compared with the unmodified starches, when they used starch modified with stearic acid containing amylose-lipid complexes, as a fat-replacer in their formulation. They attributed the observation to the properties of the starch-lipid complex used as a fat replacer. Formation of amylose-lipid complexes results in softer non-gelling pastes (D'Silva *et al.*, 2011) by preventing the re-association of amylose molecules from forming junction zones (BeMiller & Whistler, 2009; Saha & Bhattacharya, 2010) hence retarding the gelling process.

The rheological differences between the emulsions containing starch/stearic acid and starch/monoglyceride are related to different ability of various lipids to complex with amylose (Kaur & Singh, 2000). Long-chain saturated fatty acids such as stearic acid, form amylose-lipid complexes more readily compared to the monoglyceride (Tufvesson, Wahlgren & Eliasson, 2003; Putseys *et al.*, 2010). Thus available uncomplexed/partially complexed amylose, in the case of the monoglyceride, can associate with each other to form junction zones and thus higher amount of molecular entanglement (BeMiller & Whistler, 2009) leading to higher viscosity. Polymers with more junction zones are more rigid and rebuild their structure less easily when disturbed by shearing force (Saha & Bhattacharya, 2010), which would explain the higher zero shear viscosity between the two emulsions; starch/monoglyceride in comparison to starch/stearic acid.

All tested emulsions had clear shear-thinning characteristics. Shear-thinning occurs when there is a breakdown of structural units in food during shearing and particles orientate along the shear direction, minimising resistance to flow (BeMiller & Whistler, 2009; Rao, 2007). For thixotropic shear-thinning fluids, when the concentration or molecular weight increases, flow behaviour index (n) decreases, but the consistency coefficient (K) increases (Kasapis & Bannikova, 2017). This trend was observed with all the reduced-fat mayonnaise-type emulsions formulated with the different fat replacers as their concentrations increased along with increasing fat-replacement level (Table 3.2.8). Mun *et al.* (2009) and Teklehaimanot *et al.* (2013) also reported a decrease in flow behaviour index with an increasing consistency coefficient (K) for all the reduced-fat mayonnaise-type emulsions investigated. Shear-thinning is often exhibited by emulsions that contain particles (e.g., droplets, crystals, or biopolymers) that are aggregated by weak forces (McClements, 2005). During the shearing process, the aggregated particles present in the emulsion deform and disrupt and eventually reduce the emulsion's resistance to flow, resulting in a reduction in its apparent viscosity over time.

Starch-lipid complexes have the ability to increase viscosity during pasting (D'Silva *et al*., 2011; Maphalla & Emmambux, 2016). Hence, the addition of the complexes as fat-replacers, consequently, increased the viscosity of the continuous phase of the reduced-fat emulsions. This leads to an increase in the energy needed to rebuild their network structure, hence their high hysteresis area. Tárrega, Durán and Costell (2004), suggested a possible relationship between the viscosity and hysteresis of a thixotropic fluid, i.e. the higher the viscosity, the larger the hysteresis. The viscous nature of the reduced-fat emulsions containing starch/monoglyceride probably contributed to the higher hysteresis values.

In the rheological and tribological experiments, samples were not tested in the presence of saliva that affects food emulsions during oral processing. Food emulsions are prone to flocculation and destabilisation as a result of mixing with saliva and oral shearing (van Aken, Vingerhoeds & de Hoog, 2005; Silletti, Vingerhoeds, Norde & Van Aken, 2007; Sarkar and Singh 2012). The droplet destabilisation process, which affects lubrication, is dependent on their charge status in an emulsion and is critical for their oral stability (Silletti *et al.*, 2007). A non-flocculated emulsion would normally be perceived as smooth and creamy, but a flocculated emulsion would often be sensed as rough and dry with probably increased thickness sensation (Vingerhoeds, Silletti, De Groot, Schipper & Van Aken, 2009) and severe flocculation could lead to coalescence of oil droplets which could be perceived as a greasy or oily emulsion (Chen, 2015). In the study, all the samples were perceived as highly smooth and creamy (Table 3.2.6), possibly indicating the absence of flocculated droplets.

Presence of saliva might affect the perception of food also through the action of salivary enzymes. Lubrication of starch-based fat-reduced food exposed to salivary amylase was studied by de Wijk and Prinz (2005), showing the break-down of food matrix and fat-release. The corresponding effect is not expected in test samples since the preparation process of the amylose-lipid complexes used in the study results in the formation of highly crystalline and digestion resistant starches (D'Silva *et al*., 2011; Maphalla & Emmambux, 2016; Cuthbert *et al.*, 2017).

3.2.5 Conclusions

Maize starch modified with 2 % monoglyceride, as a fat replacer can be used to replace up to 98 % of sunflower oil in reduced-fat mayonnaise-type emulsion production without significantly compromising important in-mouth textural sensory perceptions of smoothness, creaminess, melting and mouth-coating. Thickness and mouth-coating ratings as sensory properties can be correlated with measured rheological properties and attributed to the availability of uncomplexed amylose, which is more abundant in the starch/monoglyceride fat-replacer than in starch/stearic acid one, to form junction zones and molecular entanglements; Perceptions of creaminess and oiliness have been correlated with tribological properties and attributed to the ability of the modified starches containing amylose-lipid complexes to stabilise (remaining) oil droplets in the food emulsions matrix against coalescence. Thus sensory properties are a combination of the rheology and tribology properties of the reduced-fat mayonnaise-type emulsion.

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3.3 EFFECT OF SUBSTITUTING SUNFLOWER OIL WITH LIPID-MODIFIED MAIZE STARCH FAT REPLACERS ON ACCELERATED (40 °C WITH 24 H UV ILLUMINATION) SHELF LIFE AND CONSUMER ACCEPTANCE OF MAYONNAISE-TYPE EMULSIONS

Abstract

Survival analysis based on consumers' acceptance or rejection was used to estimate the shelf-life of reduced-fat mayonnaise-type emulsions produced by substituting sunflower oil with lipid-modified starch fat replacers (80 % and 98 % starch/stearic acid or 80 % and 98 % starch/monoglyceride oil replacement) of different storage times. In the study, 207 consumers evaluated reduced-fat mayonnaise-type emulsions stored at accelerated shelf-life (40 °C with 24 h UV illumination). Consumers answered a "yes" or "no" question regarding the intention to buy or consume the reduced-fat mayonnaise-type emulsions. Also, the oxidative stability of the reduced-fat mayonnaise-type emulsions during storage was determined. The peroxide values of all the reduced-fat mayonnaise-type emulsions significantly decreased ($p < 0.05$) with accelerated storage while p-Anisidine values increased. The acceptability of all the products reduced with storage time. At 50 % probability of consumer acceptance, the reduced-fat mayonnaise-type emulsion containing 80 % starch/monoglyceride was the most acceptable of the experimental products and had a predicted accelerated shelf-life beyond 35 storage days. The emulsions containing 98 % starch/stearic acid had the least shelf life of about 7.5 days. The total rate of oxidative rancidity increased with accelerated storage.

3.3.1 Introduction

Mayonnaise, a semi-solid oil-in-water emulsion is typically described as a high-fat and high-calorie food (Mun *et al*., 2009; Lee *et al*., 2013). Commercial mayonnaise typically contains oil, vinegar, egg yolk, salt, thickening agents, and flavourings (Smith & Hui, 2008). The United States law requires that mayonnaise contains not less than 65 % vegetable oil by weight (U. S. Code of Federal Regulations, 2006). In South Africa, mayonnaise should contain at least 52 % edible vegetable oil by volume while reduced oil mayonnaise shall contain between 25 % and 39 % edible vegetable (RSA, 2000).

Mayonnaise, (Su, Lien, Lee & Ho, 2010), is consumed worldwide and available in most homes as a convenient food product. On the other hand, consumer awareness of the adverse effects of excessive intake of dietary fat is increasing, and health-conscious individuals are modifying their dietary habits and eating less fat (Kearney, 2010). Vorster *et al*. (2013) reported an alarming increase in the prevalence of diet-related chronic diseases due to diet and lifestyle changes. The timely interventions by the food industry and researchers to develop reduced-fat products have been a step in the right direction. However, consumers do not only ask for reduced-fat foods, but their demand for 'clean labels' on food continues to increase as well (Chareonthaikij *et al*., 2016).

In previous studies, two lipid-modified starch-based fat replacers containing amylose-lipid complexes (maize starch with 1.5 % stearic acid and maize starch with 2 % monoglyceride) were characterised. The impact of substituting sunflower oil in reduced-fat mayonnaise-type emulsions with these starch-based fat-replacers on the sensory, lubricating and rheological properties of the emulsions was also researched. Lipid-modified starches were non-gelling and exhibited fat-like properties such as good lubricity, glossiness, smoothness, and creaminess (research chapter 1). All the reduced-fat mayonnaise-type emulsions formulated using the lipid-modified starches, as a fat replacer, showed good lubricating properties similar to that of full-fat emulsion (research chapter 2). The reduced-fat mayonnaise-type emulsions were smooth, creamy, melting, and ease-to-swallow. There is, therefore, the need to assess the shelf stability and consumer acceptability of these emulsions.

Commercially produced mayonnaise should be microbiologically stable at ambient storage (Smittle, 2000), due to its low pH, low water activity and the addition of preservatives (Depree &

Savage, 2001; Ma & Boye, 2013). However, changes in manufacturing processes and formulations can affect the shelf life of the products, hence the need to measure and estimate shelf life and safety. Due to the long shelf life (6–12 months) of mayonnaise at room temperature (McClements & Demetriades, 1998; Sainsbury, Grypa, Ellingworth, Duodu & De Kock, 2016), it is recommended that shelf life estimation of mayonnaise be determined by quality changes rather than microbial safety (Hough, Langohr, Gómez & Curia, 2003; Corrigan, Hedderley & Harvey, 2012). Some methods exist for determining the shelf-life of food products. These include quality-based, acceptability limit, cut-off point and survival analysis methods. Methodologies based on consumer studies are recommended for estimating the sensory shelf-life of food products (Giménez, Ares & Ares, 2012). Hence the use of survival analysis in this study.

Survival analysis is used to analysis data for which the outcome variable of interest is time until an event occurs (Giménez, 2012). Hough *et al.* (2003) used survival analysis to estimate the sensory shelf-life of food based on consumer's acceptance/rejection of stored samples. Kleinbaum and Klein (2012) defined the survivor function S(t) as the probability that a person survives longer than some specified time t: that is $S(t) = P(T > t)$. In relating this to food shelf-life studies, survivor function is defined as the probability of a consumer accepting a product beyond time *t*, that is $S(t) = P(T > t)$, assuming that the variable T is defined as the storage time at which the consumer rejects the sample (Hough *et al.*, 2003).

Consumers play a vital role in the success of a new food product, hence knowing how much a consumer likes a product, and the reason for their choice is very important. Therefore, consumers' comments should not be neglected but instead carefully analysed. Symoneaux, Galmarini and Mehinagic (2012) described comments analysis as the counting of the frequency of mention of terms used by consumers to describe a product. Many researchers have analysed consumer feedback and comments and obtained useful data about consumer perceptions of products (ten Kleij & Musters, 2003; Symoneaux *et al.*, 2012; Dietrich, Phetxumphou & Gallagher, 2014).

The need for rapid product development to meet consumer expectations, coupled with time and cost constraints associated with real-time shelf life testing (Corrigan *et al.*, 2012), have increased the importance of accelerated shelf-life tests. An accelerated test is used to obtain shelf life information by exposing products to high levels of accelerating variables such as higher temperatures, above-normal humidity, UV light exposure, higher water activity and the addition of pro-oxidants (Sainsbury *et al.*, 2016). Information obtained from the accelerated test is then extrapolated to obtain shelf-life estimates at normal levels of the accelerating variables. Acceleration storage conditions used in shelf-life testing is predetermined by the normal storage conditions peculiar to a product (Richards, De Kock & Buys, 2014). The objective of this study was to determine the effect of substituting sunflower oil with lipid-modified maize starch fat replacers on physicochemical, accelerated (40 °C with 24 h UV illumination) shelf-life and consumer acceptance of reduced-fat mayonnaise-type emulsions.

3.3.2 Materials and Methods

3.3.2.1 Preparation of mayonnaise type emulsions for shelf life

Mayonnaise-type emulsions were prepared as described in section 3.2.2.3 above.

Mayonnaise-type emulsions prepared with 80 % and 98 % sunflower oil substitution with two lipid-modified fat replacers (maize starch + 1.5 % stearic acid and maize starch + 2 % monoglyceride) were used in the shelf life study. This was done to determine consumer acceptability of reduced-fat mayonnaise-type emulsions with total percentage oil below the minimum acceptable levels (25 %) for reduced-oil mayonnaise in South Africa (RSA, 2000).

The experimental samples were each divided into 6 portions and stored for 5 weeks at weekly intervals using the reversed storage method. The reversed storage design involves all samples, each with different storage time, all available and assessed and analyzed on the same day. For the study, all the reduced-fat mayonnaise-type emulsions were prepared and stored at 4 °C. At day zero, the first batch of samples was placed into the storage chamber (Labcon laboratory equipment (PTY) LTD, South Africa) at 40 °C with 24 h UV illumination. This was followed by weekly placement of samples into the storage chamber until the 5th week. Therefore, the samples that went into the storage chamber at 0 days have the longest storage time (35 days) at accelerated conditions, with the sample that went into the storage chamber at the 5th week having the shortest accelerated storage of 7 days. The sample that remained at 4 °C during the whole period was considered as the fresh sample because it was never exposed to the accelerated conditions (40 °C with 24 h UV illumination). The full-fat mayonnaise (control) was kept at 4 °C.

3.3.2.2 Physicochemical analyses

The pH and water activity (a_w) values of the mayonnaise samples (control and stored) were measured at a temperature of 23 – 24 °C using a pH meter (Microprocessor pH 211, HANNA® products, Italy) and a water activity meter (AQUALAB Pawkit Water Activity Meter, USA), respectively. Readings were taken in triplicate.

The L*, a*, b* colour values of the mayonnaise samples (control and stored) were measured using a colour meter (Minolta Chroma meter CR-400/410, Konica Minolta Sensing, Japan), which was calibrated using a white standard porcelain plate (Y =85.7, X = 0.3166, y = 0.3242). In this colour system, L* represents the lightness and darkness, and a*and b* are the colour coordinates, whereby +a represents the red coordinate, −a is the green coordinate, +b is the yellow coordinate, and −b is the blue coordinate. The data was also represented in terms of hue angle (H) and chroma (C).

Prior to peroxide and p-anisidine values determination, lipids were extracted from the mayonnaise samples using the Folch extraction method according to Iverson, Lang, & Cooper, 2001, with some modifications. A ratio of 2:3 (v/v) of mayonnaise emulsion to chloroform: methanol (2:1v/v) mixture was vigorously mixed followed by centrifugation for 10 min at 3000 rpm. The supernatant was decanted, and the entire lower phase that contains the lipids was poured into glass beakers covered with foils and the solvent allowed to evaporate in a dark fume chamber. The lipids separated from the emulsion was stored in closed brown glass bottles at -20 °C until analyzed. Peroxide value (PV) was determined immediately after extraction according to IDF 74A: 1991 method, described by Shanta and Decker (1994). The p-Anisidine values (AV) of the samples was determined according to the AOCS Official Method Cd 18-90 (AOCS, 1999).

3.3.2.3 Consumer evaluation

Ethical approval for this study was obtained from the ethics committee of the Faculty of Natural and Agricultural Sciences, University of Pretoria, South Africa (EC170425-111).

Two hundred and seven consumers [n = 207 (76 males and 131 females)] between 18 and 36 years, who consume mayonnaise at least once a week were recruited on the University of Pretoria campus. Thirteen (13) fieldworkers were employed and given about two hours of training on how to properly recruit the right target of respondents for the study (Appendix 1).

Each field worker was responsible for recruiting 16 respondents for a particular day and time slot. Field workers used a questionnaire (Appendix 2) to screen potential respondents. They first gave the potential respondents a brief about the study and asked about their interest and willingness, and their availability to be part of the study. Based on the responses, the field worker either invited the respondent to an evaluation session or closed the interview. Respondents read and signed consent forms (Appendix 3) just before the evaluation session.

Each participant evaluated about 2 ml of each of the 12 samples of mayonnaise-type emulsions served in small polypropylene containers (35 ml volume). A 50 count per sample was obtained at the end of the evaluation. Samples were coded with randomly selected 3-digit numbers and presented in random balanced order. The containers for each consumer were placed in 12 cup muffin trays for ease of correct sample order presentations. Participants were instructed to use fresh carrot sticks to taste different samples by dipping the carrot into the sample and eating it together with the sample. They were told to expectorate samples if necessary. Participants responded “yes” or “no” to the question “Do you think a mayonnaise sample that looks, smells and tastes like (sample code), is good to eat? Consumers were told to give comments or reasons for rejecting a sample after assessing each sample when they responded ‘No’. Consumers used water to cleanse their palate. Compusense cloud software (Compusense Inc., Guelph, Canada) was used to generate codes, for the experimental design and to capture the consumers' responses. The evaluation was done over four (4) days with 52 consumers per day.

3.3.2.4 Statistical analysis

Shelf-life estimation

Survival analysis methodology was used to estimate the shelf life of mayonnaise-type emulsions using results obtained from consumers when asked if they would normally consume the samples with different storage times. Data obtained from consumers’ was transferred onto an Excel spreadsheet and censored. Due to the nature of the data obtained, interval censoring was mainly used. For example, if the consumer accepted samples stored for 0 and 2 weeks, but rejected the samples stored for 3 weeks or onwards, the time to rejection is week $2 < T \leq$ week 3. However, consumers who did not accept the control (samples stored at 4 °C) and those who answered “no” for all samples were not considered. No consumer accepted or answered ‘yes’ for samples stored for all the weeks, so no data were right-censored.

Once the censoring for each consumer had been determined, the data was fitted to the following parametric distribution models; Exponential, Weibull, Log-logistic and Log-normal to obtain precise estimates of the survival function (Kleinbaum & Klein, 2012). Shelf-life of the mayonnaise-type emulsions was estimated at the interval of 50 % probability of a consumer accepting the product (Hough, Garitta & Gómez, 2006). Calculations were performed using R statistical software [R version 3.5.1 (2018-07-02)].

Word clouds

Consumer comments for rejecting mayonnaise-type emulsions were analyzed using word clouds (https://worditout.com). In these, increasing font size indicated a greater frequency of mention of the descriptor or phrase. Comments were first streamlined to identify key descriptors and long phrases shortened. This was done because consumers' wrote their comments in a personal style without guidance. The output showed an overview of different words or phrase sizes associated with frequency of mention.

A two-way analysis of variance (ANOVA) and Fisher least significant difference test at $p < 0.05$ were used to establish the effect of the different storage times (0, 21 and 35 days) and the fat replacers (maize starch + 1.5 % stearic acid and maize starch + 2 % monoglyceride) on physicochemical (pH, water activity & colour) of the mayonnaise-type emulsions. Statistical analysis was performed using XLSTAT 2014.

3.3.3 Results

3.3.3.1 Physicochemical analysis

Table 3.3.1 shows the effect of the different fat replacers and accelerated storage period on the pH and water activity (aw) of reduced-fat mayonnaise-type emulsions. The pH for all the reduced-fat mayonnaise-type emulsions ranged between 3.80 and 3.86 and was significantly higher ($p < 0.05$) than the pH of the full-fat control mayonnaise. Accelerated storage did not significantly affect ($p > 0.05$) the pH of the reduced-fat mayonnaise-type emulsions. Addition of the different fat replacers significantly increased ($p < 0.05$) the water activity of all the reduced-fat mayonnaise-type emulsions. However, changes observed during the storage period were not significant ($P > 0.05$).

The combined effect of the different fat replacers and storage conditions on the colour parameters of the reduced-fat mayonnaise-type emulsions are presented in Table 3.3.2. Generally, accelerated storage did not affect ($p > 0.05$) the appearance of the reduced-fat mayonnaise-type emulsions. Nonetheless, the chromaticity, C, of all the reduced-fat emulsions at 98 % oil replacement was mostly higher compared to all the reduced-fat mayonnaise-type emulsions at 80 % oil replacement. Also, chromaticity at 98 % oil replacement for all the reduced-fat mayonnaise-type emulsions significantly reduced ($p < 0.05$) with storage.

Analysis of lipid oxidation parameters was determined in only the reduced-fat mayonnaise-type emulsions formulated by replacing 80 % of fat with the different fat replacers and the full-fat mayonnaise (control). This was due to difficulties encountered in the extraction of lipids from the 98 % oil replaced emulsions. The 98 % oil replaced emulsions contains only 1.4 % oil of the total emulsion in a sample size of about 400 g. Hence only small traces of oil were obtained, and these were not enough for the analysis of lipid oxidation. The peroxide values of all the reduced-fat mayonnaise-type emulsions significantly decreased ($p < 0.05$) with storage at 40 °C with 24 h UV illumination reaching the lowest values in the 5th week (Figure 3.3.1a). p-Anisidine values, on the other hand, significantly increased ($p < 0.05$) during accelerated storage in all the reduced-fat mayonnaise-type emulsions (Figure 3.3.1b). From the values calculated for total oxidation (Totox) in the reduced-fat mayonnaise-type emulsions, the rate of oxidation increased by the 3rd week of storage but decreased significantly by the 5th storage week (Table 3.3.3). At day zero, the full-fat control had a peroxide value of 3.96 meq O_2/kg oil and p-Anisidine value of 2.22. This is in comparison to the peroxide value of 5.51 meq O_2/kg oil and p-Anisidine value of 4.09 for starch/stearic acid emulsions and peroxide value of 6.04 meq O_2/kg oil and p-Anisidine value of 4.83 for starch/monoglyceride emulsions at day zero.

Table 3.3.1. Combined effect of the different fat replacers and storage period on the pH and water activity (a_w) of reduced-fat mayonnaise-type emulsions at different accelerated storage days

Mayonnaise samples	*Storage period (days)*	*pH*	a_w
Full-fat (no fat replacer)	(Control)	$3.72^{d} \pm 0.0$	$0.93^{f} \pm 0.0$
80 % maize starch + 1.5 % stearic acid	0	$3.80^{c} \pm 0.0$	$0.93^{f} \pm 0.0$
	21	$3.80^{c} \pm 0.0$	$0.95^{e} \pm 0.0$
	35	$3.82^{abc} \pm 0.0$	$0.97^{d} \pm 0.0$
98 % maize starch + 1.5 % stearic acid	0	$3.81^{bc} \pm 0.0$	$0.97^{d} \pm 0.0$
	21	$3.84^{ab} \pm 0.0$	$0.95^{e} \pm 0.0$
	35	$3.83^{abc} \pm 0.0$	$0.97^{d} \pm 0.0$
80 % maize starch + 2 % monoglyceride	0	$3.81^{bc} \pm 0.0$	$0.97^{cd} \pm 0.0$
	21	$3.84^{ab} \pm 0.0$	$0.98^{bcd} \pm 0.0$
	35	$3.84^{ab} \pm 0.0$	$0.99^{ab} \pm 0.0$
98 % maize starch + 2 % monoglyceride	0	$3.82^{abc} \pm 0.0$	$0.99^{ab} \pm 0.0$
	21	$3.86^{a} \pm 0.0$	$0.99^{a} \pm 0.0$
	35	$3.84^{ab} \pm 0.0$	$0.98^{abc} \pm 0.0$

- Values are mean of triplicate experiments with standards deviation.
- Mean values in the same column with different superscripts are significantly different at $p < 0.05$

Table 3.3.2. Combined effect of the different fat replacers and storage period on the colour parameters of reduced-fat mayonnaise-type emulsions at different accelerated storage days

Mayonnaise samples	***Storage period (days)***	***L***	***a***	***b***	***C***	***h***
Full-fat (no fat replacer)	**(Control)**	79.41^{d} ±0.2	-0.66^{c} ± 0.1	20.47^{a} ± 0.4	20.47^{a} ± 0.4	91.85^{cd} ± 0.3
80 % maize starch + 1.5 % stearic acid	**0**	79.31^{de} ± 1.4	-1.56^{e} ± 0.3	16.01^{c} ± 2.1	16.09^{c} ± 2.1	95.72^{a} ± 1.8
	21	78.64^{def} ± 0.9	-1.25^{de} ± 0.3	16.22^{c} ± 1.8	16.27^{c} ± 1.8	94.51^{a} ± 1.6
	35	78.26^{efg} ± 1.3	-1.25^{de} ± 0.4	16.14^{c} ± 2.1	16.19^{c} ± 2.1	94.59^{a} ± 2.1
98 % maize starch + 1.5 % stearic acid	**0**	77.40^{g} ± 0.1	-0.41^{abc} ± 0.1	21.11^{a} ± 0.3	21.11^{a} ± 0.3	91.11^{cd} ± 0.3
	21	78.16^{fg} ± 0.2	-0.81^{cd} ± 0.1	18.54^{b} ± 0.1	18.56^{b} ± 0.1	92.50^{bc} ± 0.4
	35	78.02^{fg} ± 0.4	-0.67^{c} ± 0.3	18.22^{b} ± 0.5	18.23^{b} ± 0.5	92.11^{cd} ± 0.8
80 % maize starch + 2 % monoglyceride	**0**	84.86^{a} ± 0.5	-0.60^{bc} ± 0.4	17.04^{bc} ± 0.6	17.05^{bc} ± 0.6	92.06^{cd} ± 1.4
	21	83.09^{b} ± 0.2	-1.16^{de} ± 0.1	15.93^{c} ± 0.3	15.98^{c} ± 0.2	94.17^{ab} ± 0.3
	35	83.77^{ab} ± 0.1	-0.38^{abc} ± 0.4	18.04^{b} ± 0.5	18.15^{b} ± 0.5	91.24^{cd} ± 1.3
98 % maize starch + 2 % monoglyceride	**0**	79.62^{d} ± 0.4	-0.16^{ab} ± 0.3	20.42^{a} ± 0.1	20.42^{a} ± 0.1	90.45^{d} ± 0.9
	21	78.81^{def} ± 0.4	-0.09^{a} ± 0.3	16.23^{c} ± 0.3	16.23^{c} ± 0.3	90.32^{d} ± 0.9
	35	80.91^{c} ± 0.2	-0.52^{abc} ± 0.2	18.46^{b} ± 0.8	18.47^{b} ± 0.8	91.63^{cd} ± 0.7

- Values are mean of triplicate experiments with standards deviation.
- Mean values in the same column with different superscripts are significantly different at $p < 0.05$

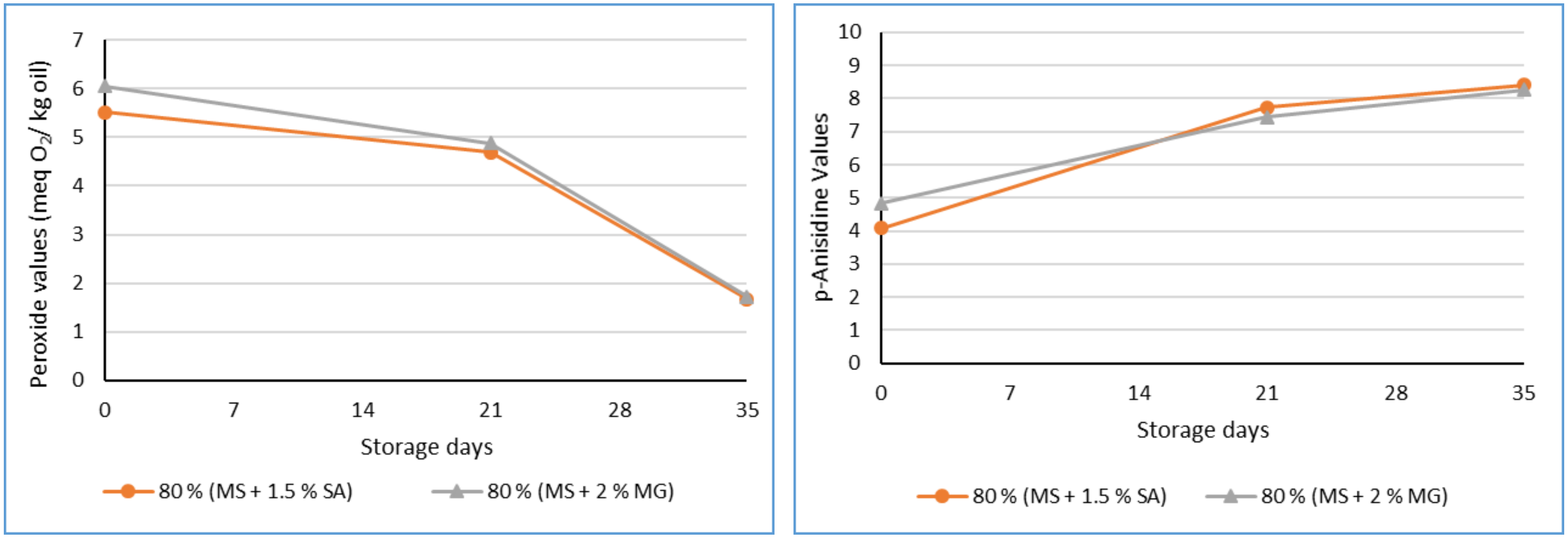


Figure 3.3.1. Chemical analyses (peroxide and p-Anisidine value) for lipids extracted from reduced-fat mayonnaise-type emulsions stored accelerated storage (40 °C with 24 h UV illumination) for 35 days

Table 3.3.3. Combined effect of the different fat replacers and storage period on Total oxidation value (Totox value)

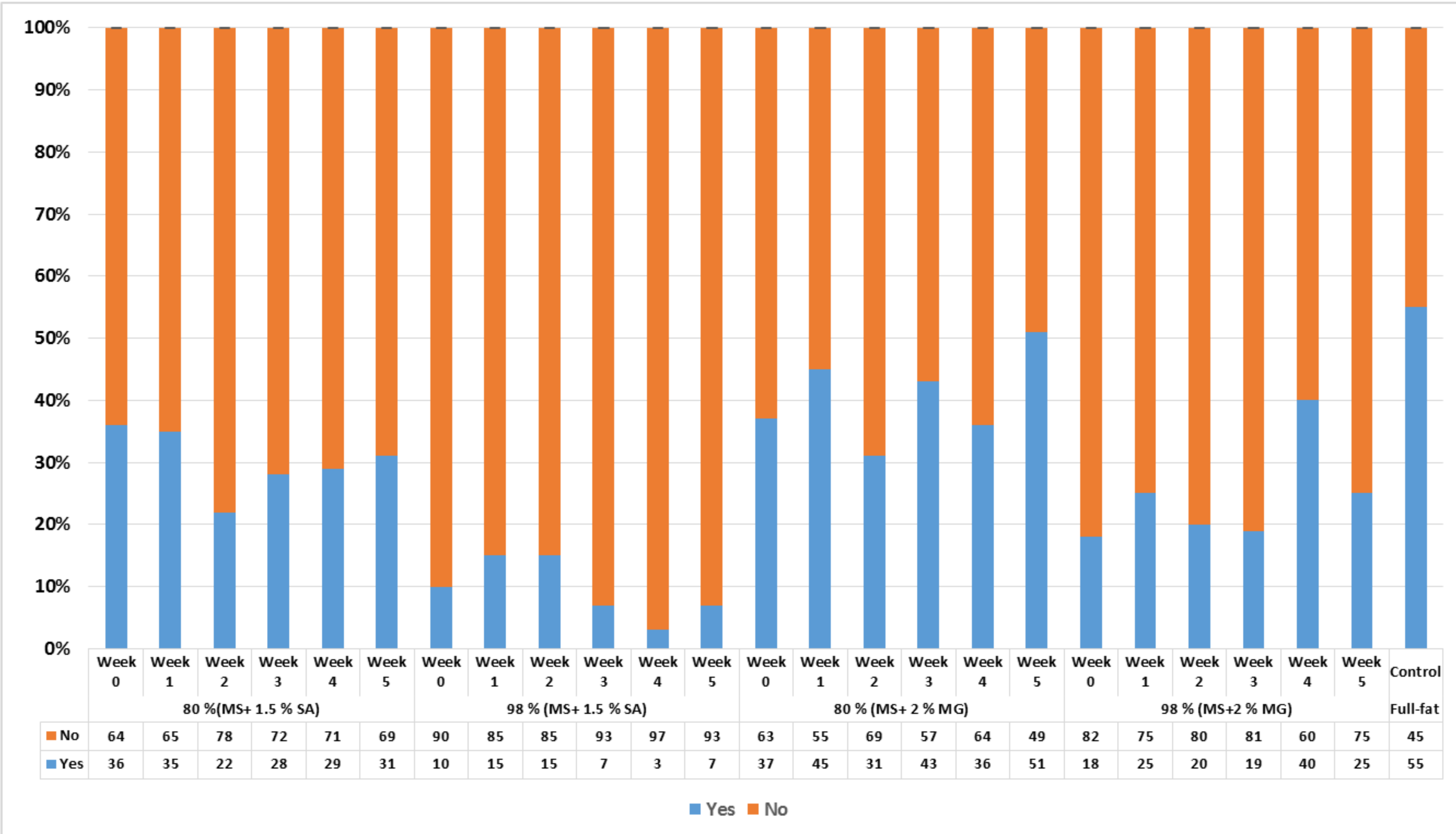
Mayonnaise samples	*Storage period (days)*	*Totox value (2PV + AV)*
Full-fat (no fat replacer)	0	10.14^{c} ±0.51
	0	13.75^{abc} ±1.95
80 % maize starch + 1.5 % stearic acid	21	17.11^{a} ±3.19
	35	11.77^{bc} ±1.88
	0	15.31^{ab} ±3.82
80 % maize starch + 2 % monoglyceride	21	17.20^{a} ±2.78
	35	11.70^{bc} ±1.76

- Values are mean of triplicate experiments with standards deviation.
- Mean values in the same column with different superscripts are significantly different at $p < 0.05$
- PV – Peroxide value, AV – p-Anisidine value

3.3.3.2 Consumer evaluation

Percentage consumer acceptance/rejection

Figure 3.3.2 shows a plot of the consumer acceptance/rejection percentages for the different reduced-fat mayonnaise-type emulsions at different storage periods (weeks). The plot shows that consumers acceptance or rejection of the samples did not follow any trend and was not dependent on storage time. Consumers rejected some fresh samples stored at 4 °C but accepted the same samples in the 5th week of storage. Total acceptance of the full-fat control (fresh) at 4 °C was 55 %. In comparing the average acceptance (%) of the reduced-fat mayonnaise-type emulsions to the full-fat, the reduced-fat emulsions with 80 % starch/monoglyceride were accepted approximately 1.4 times less. While the emulsion formulated with 98 % starch/stearic acid was accepted 6 times less. (Table 3.3.4).



	80 %(MS+ 1.5 % SA)						98 % (MS+ 1.5 % SA)						80 % (MS+ 2 % MG)						98 % (MS+2 % MG)						Full-fat
	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5	Control
No	64	65	78	72	71	69	90	85	85	93	97	93	63	55	69	57	64	49	82	75	80	81	60	75	45
Yes	36	35	22	28	29	31	10	15	15	7	3	7	37	45	31	43	36	51	18	25	20	19	40	25	55

Figure 3.3.2. A plot showing percentages of consumer acceptance/rejection of the different reduced-fat mayonnaise-type emulsions at different accelerated storage periods (weeks)

- MS (maize starch) – SA (stearic acid) – MG (monoglyceride)

Table 3.3.4. Percentage acceptance of reduced-fat mayonnaise-type emulsions relative to percentage acceptance of full-fat (control)

Mayonnaise samples	*Acceptance of samples (%)*
Full-fat (no fat replacer)	55
80 % maize starch + 1.5 % stearic acid	30
98 % maize starch + 1.5 % stearic acid	10
80 % maize starch + 2 % monoglyceride	40
98 % maize starch + 2 % monoglyceride	25

Consumer rejection comments

From the word cloud outputs (Figure 3.3.3a-e), reasons for rejection was described based on aroma, appearance and flavour attributes. The following descriptors were mainly used as a reason for rejecting the full-fat control; tastes-bad, oily, looks bad, vinegar smell and watery.

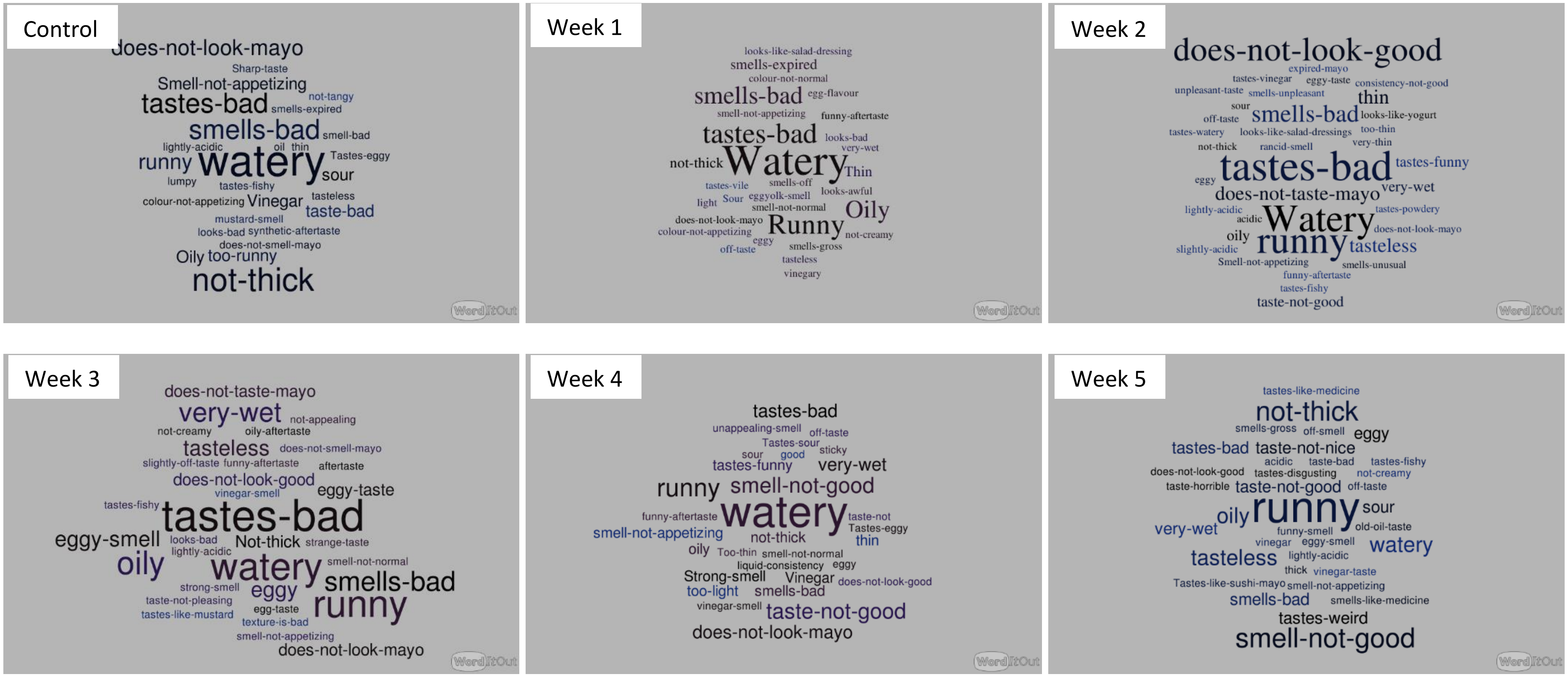
The appearance of the reduced-fat mayonnaise-type emulsion formulated with 80 % starch/stearic acid, throughout the storage period, was mainly the reason for rejection for most of the consumers. They described the samples as being watery, runny, very wet, thin, and not looking good like standard mayonnaise. Consumers also described the samples as having a bad taste, bad smell and as being oily.

The reduced-fat mayonnaise-type emulsion formulated with 98 % starch /stearic acid was the least liked and received the most negative comments. Samples were described and rejected on similar grounds (described as being watery, runny, tasting and smelling bad) as the mayonnaise formulated with 80 % starch/stearic acid. However, one unique characteristic that formed a basis of rejection for this reduced-fat emulsion was the presence of water separating from the emulsion, which most consumers described as ‘water oozing out of product’ (Figure 3.3.4).

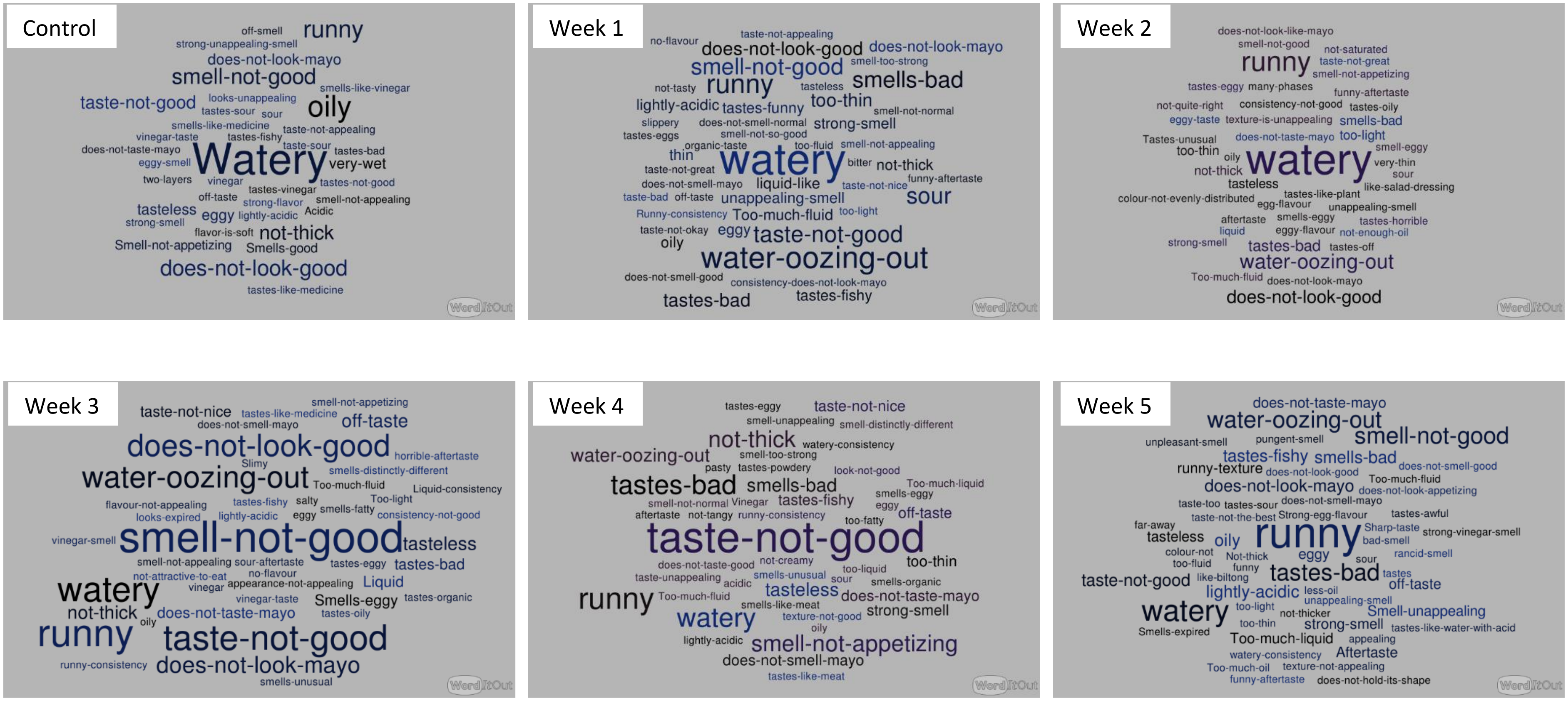
The reduced-fat mayonnaise-type emulsion formulated with 80 % starch/monoglyceride, had the least negative comments and was mainly rejected based on its appearance and in-mouth texture attributes. Consumers described the samples as not looking good and being thick and lumpy. Other rejection descriptors that also showed up included; vinegar smell, eggy smell and flavour, sour, off-taste, and the fact that the samples smelled and tasted bad.

Lastly, the reduced-fat mayonnaise-type emulsion formulated with 98 % starch/monoglyceride was described as being thick, lumpy, having a vinegar smell, eggy taste, eggy flavour, and generally having bad smell and taste. The samples were also described as having an off-taste and as being expired.

(a) Word clouds of reasons given for rejecting full-fat mayonnaise (without fat replacer)



(b) Word clouds of reasons given for rejecting reduced-fat emulsions with 80 % (starch/stearic acid)



(c) Word clouds of reasons given for rejecting reduced-fat emulsions with 98 % (starch/stearic acid)

(d) Word clouds of reasons given for rejecting reduced-fat emulsions with 80 % (starch/monoglyceride)

(e) Word clouds of reasons given for rejecting reduced-fat emulsions with 98 % (starch/monoglyceride)

Figure 3.3.3 (a - e). Word clouds of reasons given for rejecting full-fat mayonnaise (without fat replacer) and reduced-fat mayonnaise-type emulsions

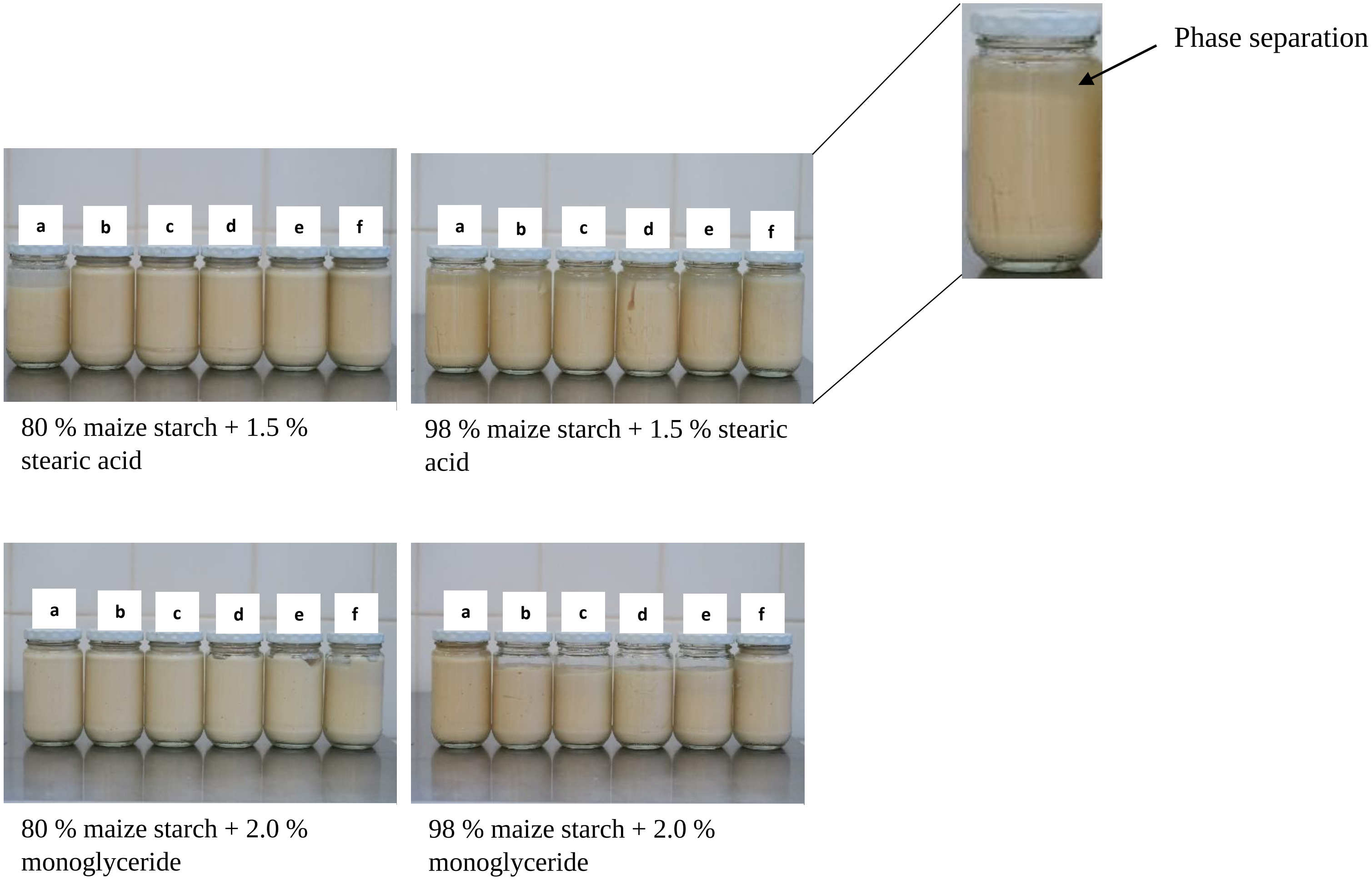


Figure 3.3.4. Photos of reduced-fat mayonnaise-type emulsions after accelerated storage

(a) Control samples stored at 4 °C, (b) samples stored at accelerated conditions (40 °C + 24 h fluorescent illumination) for 7 days, (c) samples stored at accelerated conditions (40 °C + 24 h fluorescent illumination) for 14 days, (d) samples stored at accelerated conditions (40 °C + 24 h fluorescent illumination) for 21days, (e) samples stored at accelerated conditions (40 °C + 24 h fluorescent illumination) for 28 days, (f) samples stored at accelerated conditions (40 °C + 24 h fluorescent illumination) for 35 days.

3.3.4 Discussion

The relatively lower pH is possibly due to the absence of modified starch in the full-fat mayonnaise, and the relatively higher pH was due to dilution of acetic acid in the aqueous phase as a result of the reduction of oil and the addition of the modified starches in the case of the reduced-fat mayonnaise-type emulsions. Worrasinchai *et al*. (2006), reported a similar range of pH values (3.80–3.85) for reduced-fat mayonnaise-type emulsions. An increase in water activity of all the reduced-fat mayonnaise-type emulsions can be due to the increase in the aqueous phase with the addition of the modified starches. Available amylopectin fractions in the modified starches possibly recrystallised during storage (BeMiller, 2011), thus increasing the available water. Reassociation and crystallisation of amylopectin molecules during the process of retrogradation involves phase separation of water (syneresis) (BeMiller & Whistler, 2009).

The increase in colour intensity observed mainly at 98 % oil replacement could be attributed to a decrease in droplet concentration resulting in increased absorption of light waves (Chantrapornchai, Clydesdale & McClements, 1999; Chantrapornchai, Clydesdale & McClements, 2000; McClements, 2005). A lower droplet concentration causes light waves to penetrate further into an emulsion, increasing light absorption, hence increasing the colour intensity of the emulsion (Chantrapornchai *et al*., 1999; Chantrapornchai *et al*., 2000; McClements, 2005). A similar trend has been reported by other researchers (Chantrapornchai *et al*., 1999; Worrasinchai *et al*., 2006; Mun *et al.*, 2009) when they produced reduced-fat mayonnaise-type emulsions.

Peroxide and p-Anisidine values were measured to determine the initial and later-stage products formed by lipid oxidation in the emulsions, respectively (Hsieh & Regenstein, 1992). Peroxide values are a measure of the amount of liberated iodine after peroxides formed in the emulsions oxidizes potassium iodide (KI). While the p-Anisidine value estimates the amount of α- and β-unsaturated aldehydes (mainly 2-alkenals and 2, 4 - dienals), which are secondary oxidation products in fats and oils (Nielsen, 2010). Edible commercial oils usually have an acceptable peroxide limit of 10 meq active oxygen per kg of oil (Viau, Genot, Ribourg & Meynier, 2016). Also, peroxide values >20 are indicative of very poor quality fats and oils, which generally would have significant off-flavours (Nielsen, 2010). All the reduced-fat mayonnaise-type emulsions had peroxide values below 10 meq O_2/kg of oil, but the p-Anisidine and Totox values increased during storage. This suggests that the peroxide values were not a good indicator of the rate of oxidation. The decline in the peroxide values and increase in p-Anisidine values with storage can be attributed to the possible conversion of the primary oxidation products to secondary oxidation products. In the propagation stage of lipid oxidation in emulsions, the primary oxidation products, lipid hydroperoxides (ROOH) are decomposed into highly reactive peroxyl (ROO*) and alkoxyl (RO) radicals by transition metals or pro-oxidants. These radicals react with unsaturated lipids within the droplets or at the oil-water interface, which leads to the formation of lipid radicals. These lipid radicals, in turn, react with other lipids in their immediate vicinity. Formation of alkoxyl radicals leads to β-scission reactions that result in the generation of secondary oxidation products (hydrocarbons, alcohols, aldehydes, ketones, volatile organic acids and epoxy compounds), which are responsible for the characteristic physicochemical and sensory properties of oxidised oils (McClements & Decker, 2000; Gorji *et al*., 2016). The effect of storage time found in this study has also been reported in other studies.

The increasing rate of total oxidation (Totox) recorded in all the reduced-fat mayonnaise-type emulsions can be attributed to the accelerated storage conditions. That is exposure to high temperature (40 °C) and 24 h UV illumination. Several researchers report the effect of high temperature on the rate of lipid oxidation. Lipid oxidation in fish oil-enriched light mayonnaise increased with storage temperature (Sørensen, Nielsen & Jacobsen, 2010); total oxidation and peroxide values were higher in mayonnaises stored at 25 °C compared with samples stored at 4 °C (Li *et al*., 2014). In a study to investigate the oxidation stability of cholesterol in mayonnaise during storage, although the oxidation rate generally increased during storage, the total cholesterol oxides formed at 25 °C were higher than at 4 °C (Morales-Aizpurúa & Tenuta-Filho, 2005).

UV radiation spans the wavelength region from 100 to 400 nm (Diffey, 2002; Guerrero- Beltr·n & Barbosa-C· novas, 2004). Lipids present in foods undergo oxidative deterioration when exposed to both ultraviolet radiation and visible light due to photosensitised oxidation (Lennersten & Lingnert, 2000). Sensitiser compounds present in the food are converted to an excited state when light energy is absorbed. The excited sensitiser then reacts with the lipid during the formation of free radicals, leading to the formation of highly reactive singlet oxygen (Lennersten & Lingnert, 2000; Gorji *et al.*, 2016). The rate of lipid oxidation was accelerated in the order 365 nm > 405 nm > 435 nm, when low-fat mayonnaise was exposed to UV wavelengths shorter than 470 nm (Lennersten & Lingnert, 2000). Fatty acids are not absorbed in the ultraviolet region below 470 nm (Lennersten & Lingnert, 2000); therefore, mayonnaise must be protected against wavelengths shorter than 470 nm to prevent the occurrence of light-induced lipid oxidation.

It can, therefore, be suggested that the presence of the modified starches could not effectively retard the rate of lipid oxidation as was expected. Biopolymers have been found to inhibit lipid oxidation in oil-in-water emulsions, which has been attributed to free radical scavenging, transition metal binding, and viscosity enhancement (Shimada *et al*., 1992; Matsumura *et al*., 2003; Paraskevopoulou, Boskou & Paraskevopoulou, 2007; Chen, McClements & Decker, 2010). The presence of egg yolk in the aqueous phase as a stabiliser, possibly introduced iron ions, Fe^{2+} that promoted and accelerated the oxidation process. Jacobsen *et al*. 2001, proposed that iron bridges between egg yolk proteins low-density lipoproteins, lipovitellin and phosvitin at the oil-water interface are broken at low pH (4) causing iron ions, Fe^{2+} to be liberated and thus initiate the lipid oxidation process. Also, the modified starches possibly could not effectively stabilise the droplets by forming a thick hydrophilic polymeric coating around it. Hence the oil droplets could easily interact with the aqueous phase pro-oxidants, thus increasing the rate of oxidation. Accelerated lipid oxidation requires that the pro-oxidants come into close contact with the lipids at the droplet surface (McClement & Decker, 2000).

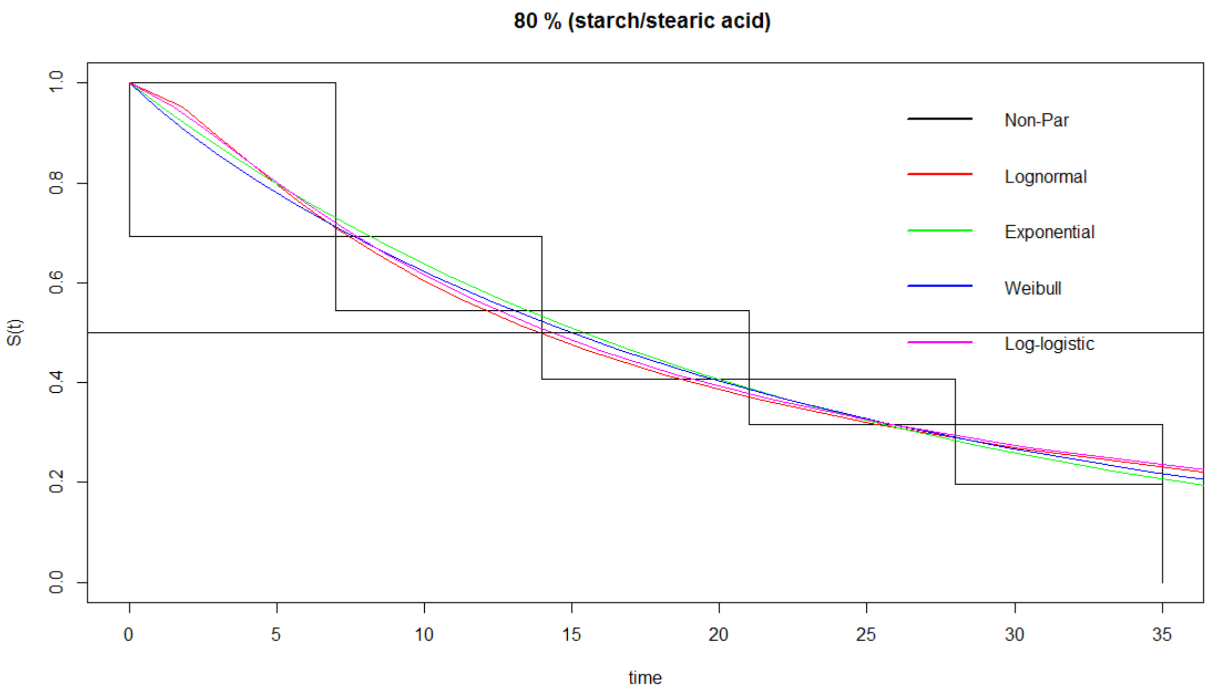
Consumers' acceptance/rejection of the reduced-fat mayonnaise-type emulsions was mainly based on the flavour, aroma, appearance and a few textural attributes. However, rejection comments from consumers were not mainly as a result of deterioration due to the storage conditions. This is because, comments such as tastes bad, smells bad, vinegar smell, 'does-not-taste-mayo', 'does-not-look-good', 'does-not-look-mayo' was attributed to the fresh samples (control). The perceived flavour attributes can be related to volatile secondary oxidation products such as aldehydes, ketones, and hydrocarbons. A few consumers' however commented on some off-flavour and attributes reminiscent of expired product, which can be associated with rancidity. It is, therefore, possible that the lipid oxidation products were below a threshold detectable by most of the consumers. A trained descriptive panel could have been best to use to assess the level of possible rancidity.

Shelf-life of the reduced-fat mayonnaise-type emulsions was determined using data obtained from the consumer evaluation. Data were subjected to the following parametric distribution models: Exponential, Weibull, Log-logistic and Log-normal and their log-likelihood compared. Log-normal distribution fitted well to the shelf-life data (Table 3.3.5), hence was used for estimating the shelf-life of the reduced-fat mayonnaise-type emulsions. Consumers were inconsistent with their feedback, probably because the samples were new experimental products. Most of the consumers responded ‘No’ to the question ‘Do you think a mayonnaise sample that looks, smells and taste like (sample code), is good to eat’? Therefore, end of shelf-life was set at the interval at which 50 % of the consumers (Cardelli & Labuza, 2001; Varela, Salvador & Fiszman, 2005; Hough *et al.*, 2006), accepted the reduced-fat mayonnaise-type emulsions based on its appearance, smell, and taste beyond which samples were rejected.

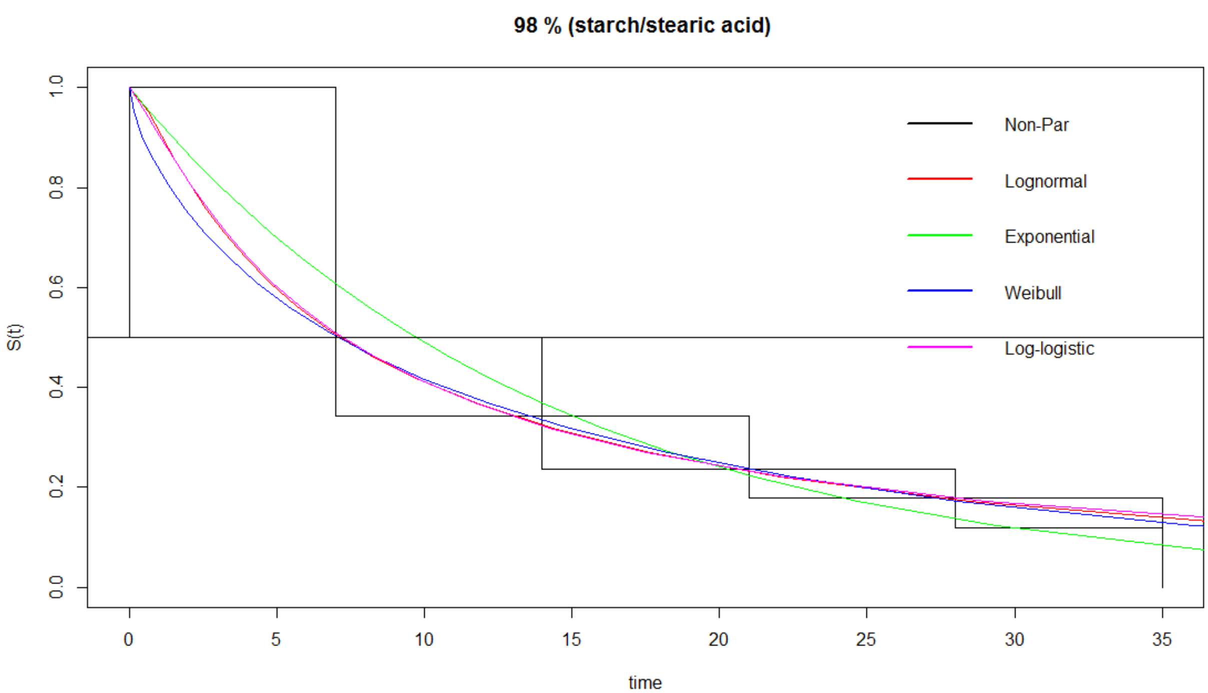
Table 3.3.5. Log-likelihood values from different parametric curves to determine the best fit to the accelerated shelf-life data on reduced-fat mayonnaise-type emulsions

Model	*Log-likelihood*
Exponential	268.89
Weibull	267.98
Log-logistic	268.88
Log-normal	268.91

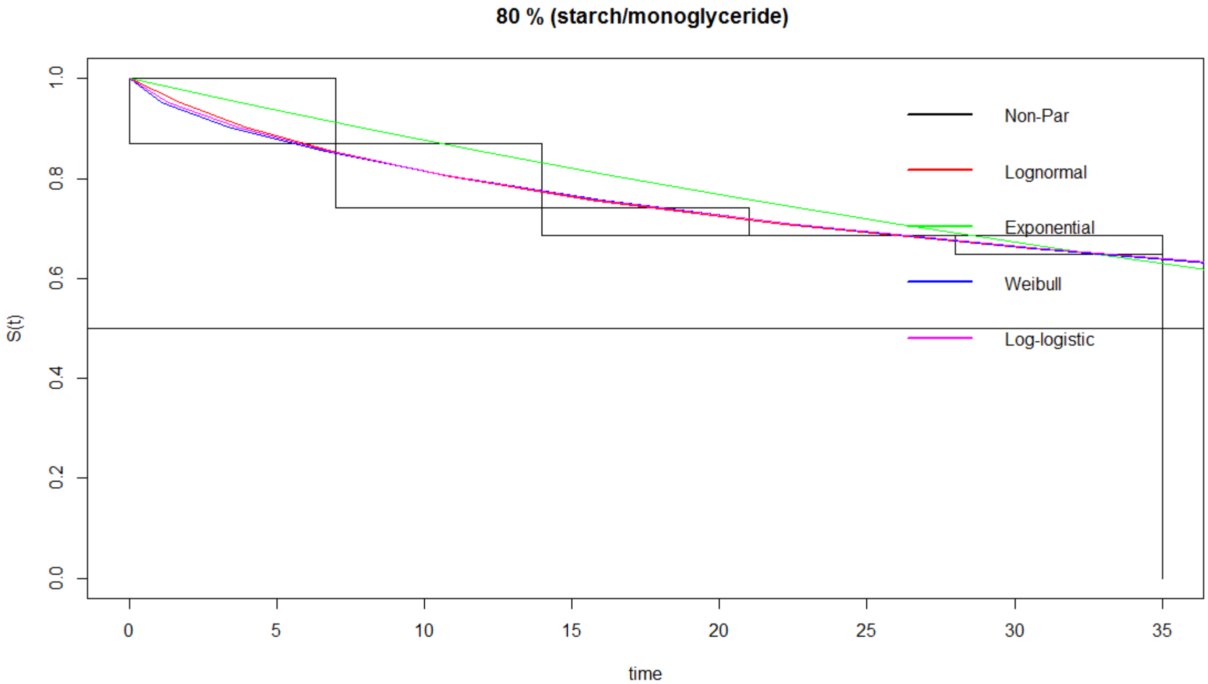
From the non-parametric modelling of the consumer data, the acceptability of all the products reduced with storage time. At 50 % probability of consumer acceptance level, the reduced-fat mayonnaise-type emulsion containing 80 % starch/monoglyceride was the most acceptable and had a predicted accelerated (40 °C with 24 h UV illumination) shelf-life beyond the 35 storage days for the study (Figure 3.3.5a-d). And the reduced-fat mayonnaise-type emulsion containing 80 % starch/stearic acid had a shelf life of about 14.5 days, samples containing 98 % starch/stearic acid had a shelf life of about 7.5 days, while samples containing 98 % starch/monoglyceride had a shelf life of about 16.5 days (Figure 3.3.5a-d). In assuming a temperature coefficient (Q_{10}) value of 2 to predict the shelf-life of the reduced-fat mayonnaise-


80 % (starch/stearic acid)
S(t)
time
Non-Par
Lognormal
Exponential
Weibull
Log-logistic

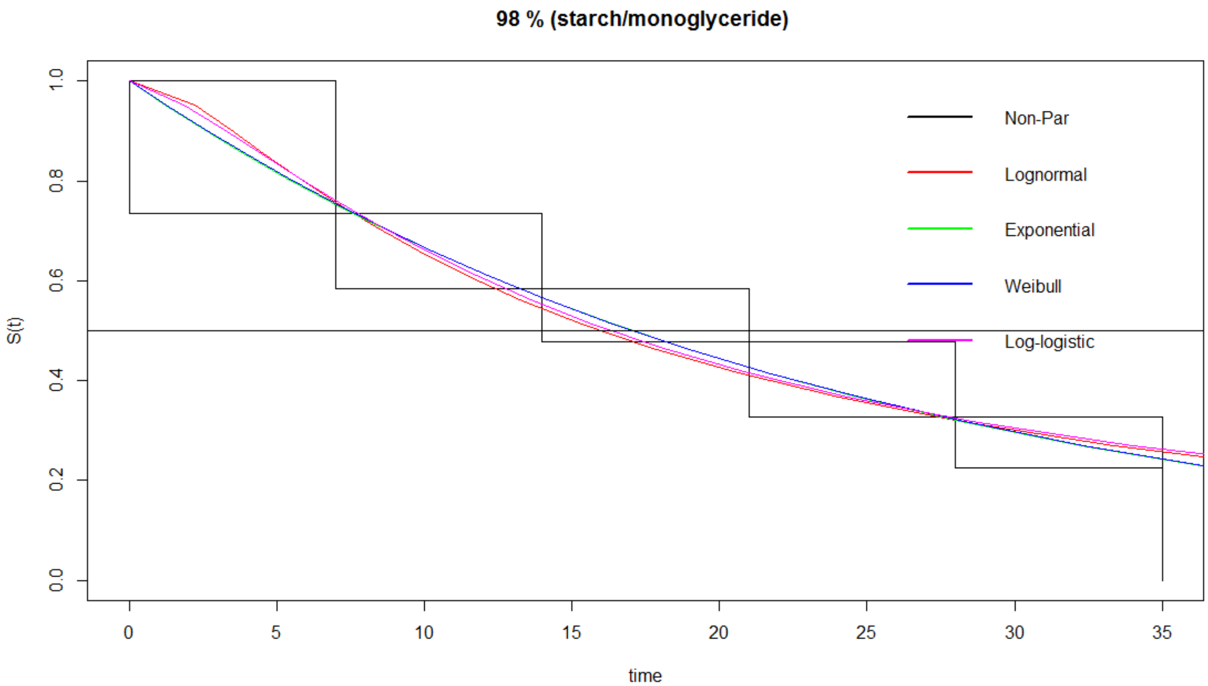
(a)


98 % (starch/stearic acid)
S(t)
time
Non-Par
Lognormal
Exponential
Weibull
Log-logistic

(b)



(c)



(d)

Figure 3.3.5 (a –d). Probability of consumer accepting the different reduced-fat mayonnaise-type emulsions compared to storage time for parametric and nonparametric estimation

-type emulsions under real-time storage conditions (ambient temperature), the minimum shelf-life of the most accepted reduced-fat mayonnaise-type emulsion would be about 140 days (4 months). And the least accepted product would have a shelf-life of 30 days (1 month). These real-time storage days are way below the expected storage days (6 - 12 months) for mayonnaise (McClements & Demetriades, 1998; Sainsbury *et al*., 2016). Further research into the oxidative stability of the reduced-fat mayonnaise-type emulsions is, therefore recommended.

3.3.5 Conclusions

The lipid-modified maize starches, as fat replacers, in the reduced-fat mayonnaise-type emulsions, does not effectively retard the rate of lipid oxidation. The increase rate of oxidative rancidity in the reduced-fat mayonnaise-type emulsions at accelerated storage may be due to the liberation of Fe^{2+} from the egg yolk present in the aqueous phase. Consumer rejection comments can be related to data obtained for oxidative rancidity determined chemically. Reduced-fat mayonnaise-type emulsions containing 80 % starch/monoglyceride is the most acceptable with an accelerated shelf-life beyond 35 storage days.

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4.0 GENERAL DISCUSSION

This section firstly critically reviews the methods used in this study. This is followed by an examination of the significant findings concerning the rheological, tribological and sensory characteristics of the reduced-fat mayonnaise-type emulsions. The final section identifies future research needs.

4.1 CRITICAL REVIEW OF METHODOLOGY

4.1.1 Preparation of fat replacers

Concerns about consumer and environmental safety related to the use of chemicals (Zia-ud-Din *et al*., 2017), have encouraged the use of approved food ingredients and additives in starch modification process and the development of 'clean label' starches (Maphalla & Emmambux, 2016) compared to 'synthetic' chemical modification.

Due to the limitations in the physical and chemical properties of native starches in the food industry (Tovar *et al*., 2002; Singh *et al*., 2007; BeMiller, 2011; Maphalla & Emmambux, 2016), starches are modified chemically, enzymatically and physically to improve their functionalities. The latter are for example thickening, binding, mouthfeel, gelling, and water retention ability (Singh *et al.*, 2007), to enhance paste clarity and sheen, paste and gel texture, film formation and adhesion (BeMiller & Whistler, 2009) and as fat replacers (Mun *et al*., 2009; Lee *et al.*, 2013; Teklehaimanot *et al*., 2013; Ali *et al*., 2015). Of the three modification methods, physical modification that employs the use of thermal processing techniques falls more under the green chemistry methodology. Green chemistry involves molecular level research aimed at controlling chemical innovations such that, whenever possible, synthetic methodologies be designed to use and generate substances that pose little or no toxicity to human health and the environment (Poliakoff, Fitzpatrick, Farren & Anastas, 2002).

Many commercially available fat replacers, for example, Olestra, Caprenin, Salatrim and Simplesse® are chemically synthesised to achieve the desired fat-like properties (Akoh, 1998; Ognean *et al*., 2006; O'Connor & O'Brien, 2011). In this study, maize starch was modified with stearic acid and monoglyceride, classified as 'food-friendly' chemicals (Maphalla & Emmambux, 2016), by the simultaneous use of heating and shearing effects to produce amylose-lipid complexes that had fat-like properties. The resultant pastes (fat replacer) were used to replace sunflower oil in the production of reduced-fat mayonnaise-type emulsions.

It is important to note however that, these ingredients especially monoglyceride, are not accepted as ‘clean label’ in some European countries, not because they are not safe, but because they are not common everyday ingredients familiar to consumers especially with regards to their less natural-sounding name (Ingredion, 2014). Also, the chemical process involved in the production of these ‘food-friendly’ chemicals in the industrial further make them unacceptable as ‘clean label’. Monoglyceride is produced from the esterification reaction between a triglyceride with glycerol. Stearic acid is obtained from fats and oils by the saponification of triglycerides using hot water (about 100 °C). There is no definition or specific regulations/legislation on the term ‘clean label’ products (Asioli, Aschemann-Witzel, Caputo, Vecchio, Annunziata, Næs & Varela, 2017). However, Ingredion (2014), based on a consumer survey, defined ‘clean label’ as natural, organic and/or additives/preservatives free. In their study, starches, including maize starch, were generally considered natural and acceptable in nine European countries. The ‘food-friendly’ chemicals used as ingredients in the preparation of the fat replacers in this study are naturally existing food components that have been approved and utilised in the food industry. This can position the reduced-fat mayonnaise formulated in this study in the ‘clean label’ category.

The lipids (stearic acid and monoglyceride) were incorporated into the maize starch to form a homogenous mixture using absolute ethanol to ensure complete mixing of ingredients. The ethanol was then evaporated off in an oven at 40 °C because it only served as a solvent for the solutes. The limitation of this method is the use of ethanol (chemical). This would not be feasible in the industry due to the large volumes that may be involved and also the recent call for less chemical use in the food industry related to consumer and environmental safety (Zia-ud-Din *et al.*, 2017). The option of wet heat processing (pasting) the lipids and maize starches directly in a reactor could be explored.

Suspensions (10 % w/w) of the stearic acid-starch and monoglyceride-starch mixtures was wet heat processed (pasted) using a reactor (IKA® LR 1000 control). The reactor was successfully used to produce a resultant paste that contained amylose-lipid complexes (Chapter 3.1). The traditional Rapid Visco Analyser (RVA) used for wet heat processing of starches and lipids (Maphalla & Emmambux, 2016; Teklehaimanot *et al.*, 2013; D’Silva *et al*., 2011) was upscaled to the use of a reactor. One advantage of using an RVA over a reactor is that the viscosity of the pasted starch can be measured during heat processing in the RVA whilst this is not possible with the reactor. However, the RVA has a maximum canister capacity of about 50 ml compared to about 1.5 L for the reactor (Figure 4.1). This made the reactor more appropriate for use in terms of the large volume of paste required for the study. Both the RVA and the reactor have built-in mechanisms for effective heating and mixing; however, the heating and the mixing may not be exactly the same extent due to the size and volume difference. This difference may have a different reaction rate. However, both methods showed the formation of amylose lipid complexes in the modified starches that were non-gelling.

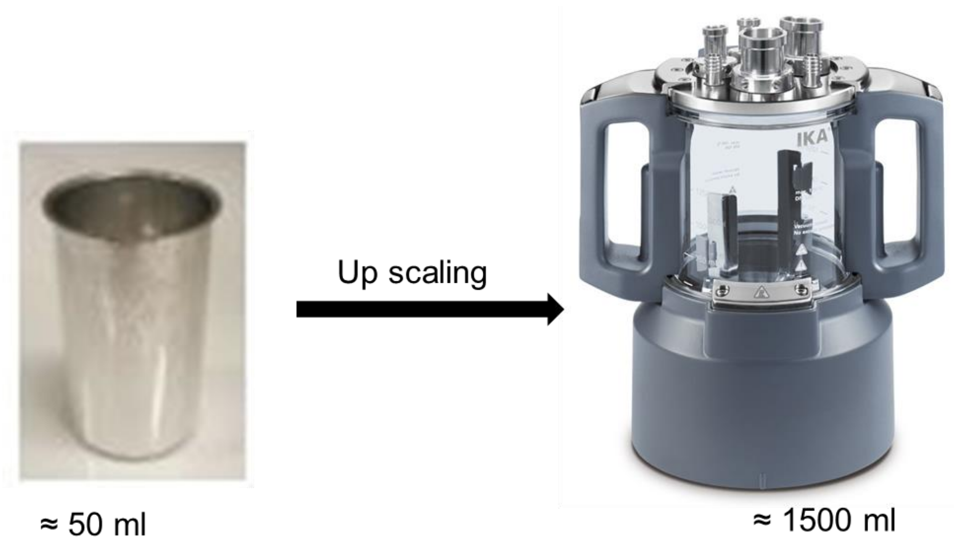

Figure 4.1. Schematic diagram showing the upscaling of the canister capacity in a Rapid Visco Analyser to a larger capacity in a rector

4.1.2 Formulation of reduced-fat mayonnaise-type emulsions

Mayonnaise emulsions were formulated by adjusting the percentage of ingredients from existing literature formulations (Su *et al.*, 2010; El-Bostany *et al.*, 2011; Teklehaimanot *et al.*, 2013). The amount of ingredients was adjusted based on the principle of Baker's percentage. This made varying the levels of ingredients (sunflower oil, egg yolk, vinegar, salt and sugar) easier to make provision for replacing some percentage of sunflower oil with freshly produced fat replacers.

In this study, modified starches were used over unmodified starches as fat replacers based on recommendations from a study by Teklehaimanot *et al.* (2013). In their study, although unmodified starch could replace up to 50 % oil in the production of low-calorie mayonnaise-type emulsions, a further increase in oil replacement resulted in a gelled mayonnaise-type emulsion that did not flow like mayonnaise compared to the emulsions formulated with modified starches. They attributed the effective use of the modified starches in the emulsion production to the formation of amylose-lipid complexes which reduces starch gel rigidity (firmness) and thus results in a non-gelling paste. It can also be suggested that the semi-crystalline nature of the amylose-lipid complexes enables it to mimic fat-like properties.

The study samples in comparison to the commercial mayonnaise references did not contain acidity regulators [(E270- lactic acid), (E330 – citric acid)], colourants [(E104 – Quinoline yellow), (E110 – sunset yellow FCF; orange yellow S)] and flavourings. Although this further positioned the formulation as 'clean label', it unavoidably became a drawback in the consumer study, especially in aspects of appearance and flavour attributes. Consumers, although not given commercial references to assess, presumably compared the study reduced-fat mayonnaise-type emulsions to prior knowledge of other commercial mayonnaise samples (Costell, Tárrega & Bayarri, 2010). This could possibly introduce some 'bias' and adversely affect the consumers' judgment for their overall acceptance of the test samples generating biased results.

4.1.3 Reversed storage design

For this study, the reversed storage design was used over the basic storage design for the accelerated shelf-life study. Unlike the basic storage design, where samples are stored at the desired temperature and periodically removed from storage for analyses, the reversed storage design involves all samples being stored at the desired temperature with different storage times but, samples are all available for analyses on the same day (Figure 4.2). One major drawback with the reverse storage design is the issue of storing control (fresh) samples. In conducting sensory shelf-life studies, it is critical to compare samples of different storage times with a sample that is considered fresh. In the study, although the fresh mayonnaise samples (control) were stored at 4 °C recommended by Martinez, Mucci, Cruz, Hough and Sanchez (1998) and Hough and Garitta (2012), some physical changes were observed in some of the samples at the end of the 5 weeks storage (Chapter 3.3). The emulsions formulated with 98 % starch/stearic acid fat replacer had some amount of water separation (syneresis). Syneresis refers to the stage during retrogradation when water molecules are squeezed out as starch polymers realign with each other. The first phase of retrogradation occurs as pasted starch starts to cool. This involves a network formation of molecular entanglement and junction zone formation between amylose molecules (Bemiller, 2011). Amylopectin entanglement may be followed at a much slower rate depending on the storage temperature. The kinetics of starch retrogradation is greatly dependent on temperature (Silverio *et al*., 2000). At low temperature down to the glass transition temperature, the rate of nucleation and propagation increases exponentially (Silverio *et al*., 2000). Therefore, for this study that involves high starch-based emulsions, the storage temperature of 4 °C for the control (fresh) samples was not appropriate.

The reversed storage design, however, has an advantage of eliminating expectation error. When assessors (trained or consumers) are called in at regular intervals to evaluate aged flavours (sour, fermented, or oxidised), they soon get the concept that they are involved in a shelf-life study (Hough, 2010). This leads them to expect the presence of aged flavours, and once found they are likely to find them for subsequent storage times repeatedly. Another advantage of the reversed storage design is that all samples are available for evaluation at the same time; hence, consumers are recruited on a single occasion to evaluate all samples.

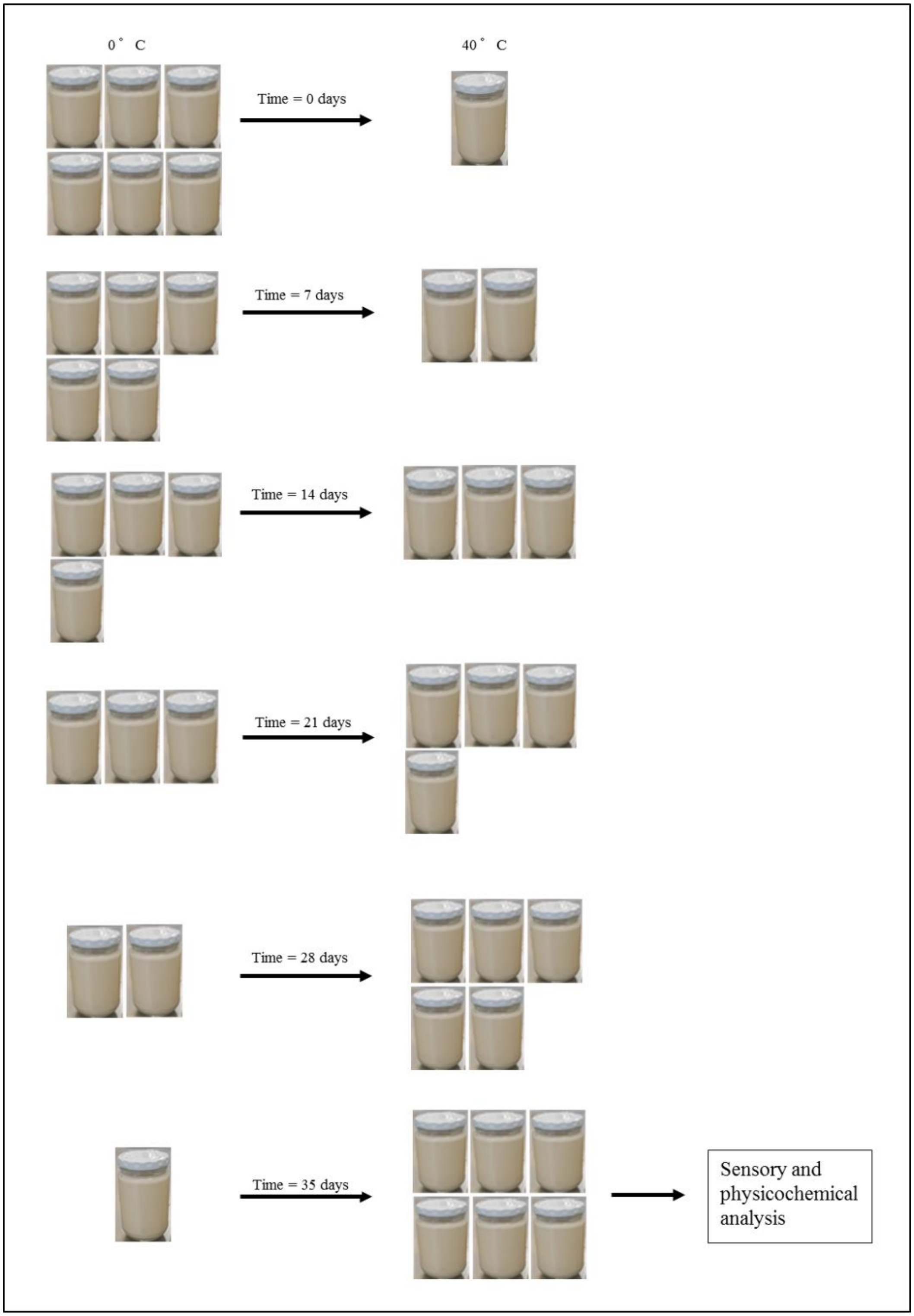

Figure 4.2. Reversed storage design used for sensory shelf-life studies of reduced-fat mayonnaise-type emulsions

Adapted from (Hough, 2010)

4.1.3 Analytical methods

4.1.3.1 Flow properties

The vane and cup were used to measure the flow properties of all the experimental samples. Samples were carefully scooped into the measuring cup to prevent disturbance of their viscosity, and allowed to equilibrate for about 5 mins to ensure uniformity in temperature before the start of the test. The rotating vane attached to the Rheometer was slowly lowered into the sample to minimize structural damage during loading.

Wall slips occur in emulsions such as mayonnaise during viscosity measurements due to the displacement of the disperse phase away from the solid boundaries e.g. the walls of the sensor system in a rheometer, leaving a depleted layer of liquid with lower-viscosity (Barnes, 1994). The low-viscosity boundary created at the wall is due to the ease of flow over the boundary as a result of lubricating effect or slips resulting in the underestimation of the fluid's viscosity. Rotating vane geometries are commonly used for their effectiveness in measuring flow properties, yield stress, and viscosity in non-Newtonian fluids (Barnes & Nguyen, 2001). The vane rheometers consist of an impeller rotating in a baffle cylinder geometry (Nazari, Moghaddam & Bousfield, 2013), that allows measurements to be made in the absence of slips (Barnes & Nguyen, 2001). For shear-thinning fluids, the fluid within the vanes moves as a solid plug and thus helps to prevent wall slip (Macosko & Larson, 1994).

4.1.3.2 Tribology measurements

The frictional and lubricating properties of the reduced-fat mayonnaise-type emulsions were measured using a mini traction machine (MTM) that is based on a ball-on-disk principle, with the sample filling the instrument compartment in which ball and disk are brought into contact and move relative to each other with different speeds entraining the sample liquid into the ball/disk contact area (Malone *et al.*, 2003b). The main parameter measured was the friction coefficient, μ, calculated as the ratio of the measured friction force and the applied normal load (Chen & Stokes, 2012). Three different lubrication regimes (boundary, mixed and hydrodynamic) were distinguished in the different tribology measurements. This gave rise to the friction coefficient vs entrainment speed curve, popularly known as the Stribeck curve (Bongaerts *et al.*, 2007a; Bongaerts, Rossetti & Stokes, 2007b).

The choice of tribo-pairs (disk and ball) made of elastomeric polydimethylsiloxane and experimental conditions (measurements at 35 ± 1 °C at sliding to a rolling ratio (SRR) set to 50 %) were aimed at mimicking the process as would occur in the oral cavity during food processing in soft contact between the tongue and soft palate. The polydimethlysiloxane is a soft hydrophobic elastomer that can easily be cast into desired surface roughness and the shape that can fit the MTM instrument set-up. Polydimethlysiloxane can be prepared with elasticity similar to that of the human tongue and is often used as a model surface material for food tribological studies (Bongaerts *et al*., 2007a; Dresselhuis, De Hoog, Stuart & Van Aken, 2008; Rossetti, Bongaerts, Wantling, Stokes & Williamson, 2009; Yakubov, Branfield, Bongaerts & Stokes, 2015; Brossard, Cai, Osorio, Bordeu & Chen, 2016). However, the polydimethlysiloxane surface is more hydrophobic than the tongue, and the disk surfaces that were used in this study had higher surface roughness than the tongue. Also, shape/aspect ratio of the surface roughness was different from that of tongue papillae. Figure 4.3 shows the surface and a cross-sectional view of a rough polydimethlysiloxane disk used in the study. Usually, smooth and rough surface are used simultaneously to cover a broad range of Stribeck curve regimes as possible. A rough surface was chosen for this study because it enables easy access to more mixed and boundary lubrication regimes that were considered relevant to the study.

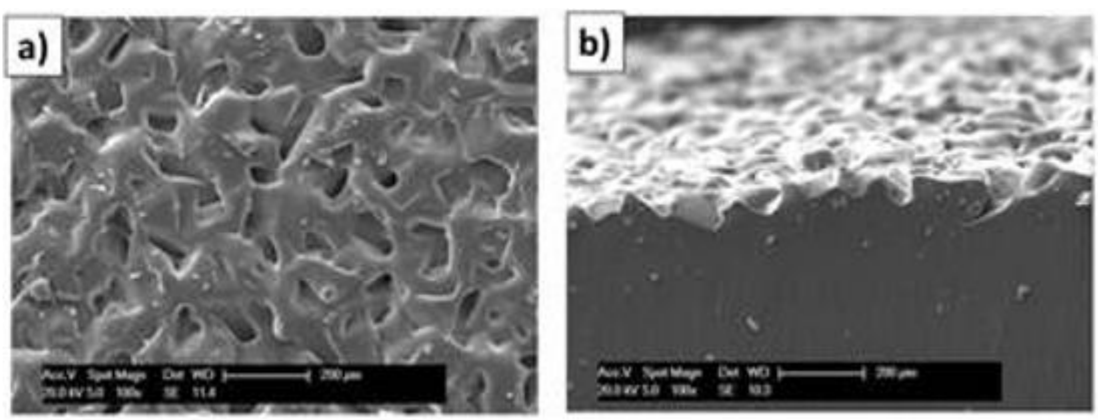

Figure 4.3. Surface of rough polydimethlysiloxane disks obtained from scanning electron microscopy. a) Top view, b) Cross-sectional view. (Magnification 100x, size of images are about 1200 x 900 µm)

One major limitation in tribology measurement by MTM is the accessibility of the different lubrication regimes with the available range of entrainment speeds available by instrument (i.e. from 1 mm/s to 1000 mm/s). It is often of interest to reach a boundary regime (surfaces in contact) or at least mixed regime (partial contact) and not only elastohydrodynamic lubrication regime, which depends only on the bulk rheological properties of the samples. To access boundary regime for the highly viscous samples used in the studies (oil, the fat replacers and the reduced-fat emulsions), polydimethlysiloxane substrates with higher surface roughness needed to be used, otherwise, if smooth substrates were used, only elastohydrodynamic regime would have been obtained. The higher the roughness, the higher is the speed at which boundary/mixed and mixed/ elastohydrodynamic lubrication transitions occur (Bongaerts *et al.*, 2007a).

For the fat replacers, it was a concentrated water-based solution of modified starch that was present in the contact area of PDMS disk and ball, while for the reduced-fat mayonnaise-type emulsion samples, it was a thin film of sunflower oil that was present in the contact area after emulsion oil droplets coalescence at the hydrophobic polydimethlysiloxane surfaces. Consequently, a boundary and mixed lubrication regimes were obtained for the fat replacers, while mixed and elastohydrodynamic regimes were obtained for the reduced-fat mayonnaise-type emulsion. This was due to the differences in the viscosity of the lubricant present in the contact area at the “effective” shear rates reached at the tested entrainment speeds, considering the rough polydimethlysiloxane substrates used in the study. At the very high effective shear rates reaching over 10 000 s^{-1} at low entrainment speeds (Bongaerts *et al.*, 2007a; Stokes, Macakova, Chojnicka-Paszun, de Kruif & de Jongh, 2011;), the shear-thinning fat replacer solutions had a lower viscosity compared to sunflower oil that is a Newtonian fluid, and its viscosity is thus independent of entrainment speed. Lubricants with lower viscosities can easily be press out from the contact area to reach a boundary regime (Stokes *et al.*, 2011; Bongaerts *et al.*, 2007a). Therefore, a boundary regime (asperity contacts) was reached for the fat replacers with low viscosity (down to 0.01 Pa.s) at the “effective” high shear rates. However, sunflower oil kept its high viscosity (0.05 Pa.s) at low entrainment speeds, and thus it was more difficult to press it out to reach the boundary regime and therefore, only mixed and elastohydrodynamic regimes were observed for the reduced-fat mayonnaise-type emulsion samples.

4.1.3.3 Sensory evaluation

Descriptive sensory

A descriptive sensory test was used to profile the fat replacers as well as the reduced-fat mayonnaise-type emulsions. The panellists were screened and selected based on their sensory acuity for discriminating tastes, aroma, texture and flavour qualities etc. This was followed by training sessions to put all personal preferences aside, adapt to an analytical frame of mind, familiarize themselves with the experimental samples and to focus on specific aspects of the product as directed by the questions and scales on the study questionnaires. A descriptive test is analytical, and a panellist is trained to give reliable information on products including quantitative and qualitative information about attributes (Stone & Sidel, 2004). One major challenge with descriptive evaluation is training the panellist to 'calibrate them' effectively for reliable results, especially with complex products, in this case, reduced-fat mayonnaise. The individual components in the emulsion give rise to different sensory sensation such as oiliness, smoothness, starchy, bitterness, etc. The components further interact with each other giving a complex sensory sensation that might be difficult to consistently and reliably evaluate. For instance, coffee has a complex flavour as a result of the interactions between volatiles developed in the coffee from cultivation, through processing to final preparation (Sunarharum, Williams & Smyth, 2014).

In a study by Elgaard, Jensen, Mielby and Byrne (2019), the researchers compared the importance of product knowledge or sensory experience on panel performance during a descriptive analysis. The researchers concluded that product knowledge was essential to obtain a "sensitive sensory profile" (descriptors that clearly and specifically define the product) for complex products, thus promoting to choose a product-specific panel (panel trained to evaluate one particular product) over a general panel (panel for all product types) for complex products. For effective calibration of a descriptive sensory panel, a product-specific panel should be trained using, e.g. the feedback calibration method (FCM) introduced by Findlay, Castura, Schlich and Lesschaeve (2006) and Findlay, Castura and Lesschaeve (2007). The feedback calibration method gives the trained panel immediate computerised feedback on their performance as compared to the conventional method were the panel receives feedback from the panel leader after each training session. The effectiveness of the rapid feedback process help to improve panel performance, ensuring a reliable sensory instrument. A limitation of the study is that the feedback calibration method, even though available as part of the Compusense software used, was not utilised during the panel training. Application of panel performance and calibration tools can contribute to the reliability of sensory results.

Consumer evaluation

Consumer acceptability is of key importance in determining product sensory shelf-life (Hough, 2010). For a consumer-based approach, it is necessary that each consumer assess all the samples with different storage times. This makes it easier to know the exact storage time at which a consumer will reject a sample. One major limitation of this approach is the introduction of assessor fatigue, especially when the research involves a large number of sample. In the study, each consumer did not assess each sample at all the storage times due to the large number of samples (30). A randomized design was adopted that ensured that all the samples were assessed an equal number of times (at least 60 times) by the end of the study. For this statistical design, 207 consumers were recruited and each evaluated 12 samples. It was established during preliminary trials that a consumer could comfortably taste and evaluate a maximum of 12 samples before sensory fatigue (i.e. decline in the quality of sensory performance) set in. For future studies, involving large sample sets, the test samples could be assessed separately in different sessions with the same group of consumers. This would afford the consumers the opportunity to assess all the samples.

The generally high levels of consumer rejections of the reduced-fat mayonnaise-type emulsions could be due to a number of reasons. Firstly, the form of presentation of the reduced-fat mayonnaise-type emulsions for testing was possibly not the ideal way of consuming mayonnaise. Regular consumers of mayonnaise will normally have it as an accompaniment of a meal and not consume only mayonnaise as was the case in this study. Eating situations significantly affect consumer acceptance (Cardello, Schutz, Snow & Lesher, 2000; Meiselman, Johnson, Reeve & Crouch, 2000). Meal context has a strong positive effect on consumer acceptance ratings (King, Meiselman, Hottenstein, Work & Cronk, 2007) and hence consumer-oriented product development must aim at placing foods within the context of meals (Miele, Di Monaco, Cavella & Masi, 2010). It would, therefore, probably have been ideal to evaluate the reduced-fat mayonnaise-type emulsions with a meal accompaniment e.g. with potato chips or in coleslaw, on their acceptability prior to the shelf-life study.

Secondly, for the study, consumers were asked to try the set of samples from different storage times and answer "yes" or "no" to the question "Do you think a mayonnaise sample that looks, smells and tastes like (sample code), is good to eat? The question positioned the reduced-fat emulsions as "mayonnaise" and this possibly affected the judgment of the consumer. Consumer acceptance of new products is generally one of dissatisfaction (Siegrist, 2008). This is because consumers' responses towards new products are greatly influenced by previous information acquired about similar products (Costell *et al*., 2010). In this study, consumers gave comments such as 'does-not-look-mayo' and 'does-not-smell-mayo' to confirm that they compared the reduced-fat mayonnaise-type emulsions to previous mayonnaise samples of their choice. The question should probably have been rephrased to read "Do you think a reduced-fat salad cream or low-fat mayonnaise or lite mayonnaise sample that looks, smells and tastes like (sample code), is good to eat?" In South Africa, emulsions with less than 52 % edible vegetable oil (maximum oil fraction in the reduced-fat mayonnaise-type emulsion was 35 %) are not classified as mayonnaise (RSA, 2000).

Thirdly, the low acceptance of the full-fat control and the fresh reduced-fat mayonnaise-type emulsions stored at 4 °C could be due to the observed physical changes that occurred during the storage, as mentioned previously (4.1.3). In hindsight, the products that separated during storage should have been considered as "failed products" and probably not have been included in the acceptability study.

4.1.3.4 Rancidity determination

The progress of lipid oxidation was determined in the stored mayonnaise samples by measuring the concentration of specific classes of reaction products or chemical changes. Peroxide and p-anisidine values were measured to determine the initial and later-stage products formed by lipid oxidation in the mayonnaise samples, respectively (Hsieh & Regenstein, 1992). One major limitation with the peroxide values determination is that peroxide compounds are only intermediate products of autoxidation and are therefore not stable. Also, higher storage temperatures cause peroxides to decompose even faster (Stansby, 1941). Therefore, although high peroxide values are a definite indication of rancid fat, moderate values are not an indication of the absence of rancidity but rather the depletion of peroxides after reaching high concentrations. Hence, the need for measurement of the p-anisidine value, which is a measure of the secondary oxidation products, such as aldehydes.

Prior to peroxide and p-anisidine values determination, lipid was extracted from the mayonnaise samples. However, initial lipid extraction experiments that involved freezing the mayonnaise samples (-20 °C for 48 h), thawing and centrifuging (7500 *g* for 10 min), was not effective. This process did not effectively breakdown and separate the emulsion it into phases. Thus, for lipid extraction, a chloroform: methanol (2:1v/v) extraction method was used (Iverson, Lang & Cooper, 2001) with some modifications. This involves a two-step principle of extraction and phase separation, where lipids are quantified in the chloroform phase. A ratio of 2:3 (v/v) of mayonnaise emulsion to chloroform: methanol mixture was vigorously mixed followed by centrifugation for 10 min at 3000 rpm instead of 5 min at 1300 *g* due to the maximum capacity of the centrifuge used. The chloroform: methanol (2:1v/v) extraction method was effective at extracting the oils because of the polarity of the solvent. Matalanis, Decker and McClements (2012) resorted to the use of chloroform: methanol method of extraction after isooctane: 2-propanol solvent failed. This is because the solvents that were less polar for lipid extraction compared to the chloroform/methanol mixture. They reported a satisfactory lipid recovery of approximately 100 per cent of the theoretical value. Chloroform: methanol extraction has also been shown to be a superior solvent, due to its greater polarity, for lipid extraction from biological tissue in several types of research (Sheng, Vannela & Rittmann, 2011; Mubarak, Shaija & Suchithra, 2015). It is also noted that the amount of extracted oil was very insignificant for mayonnaise with 98 % oil replacement and thus the rancidity test could not be carried on those samples.

4.2 RESEARCH FINDINGS

This section will discuss the rheological and tribological characteristics of the two fat replacers (maize starch modified with 1.5 % stearic acid and maize starch modified with 2 % monoglyceride) and their respective reduced-fat mayonnaise-type emulsion. The relation between these characteristics, sensory perception and influence on consumer acceptance will also be discussed.

4.2.1 High viscosity and non-gelling properties of fat replacers and reduced-fat mayonnaise-type emulsions

The fat replacers had high viscosities that decreased with increasing shear rate. Within the limit of measurement of 0.001 s-1, both fat replacers exhibited zero shear viscosities. Generally, both fat replacers were non-gelling, paste-like and contained amylose-lipid complexes (Chapter 3.1). All the reduced-fat mayonnaise-type emulsions showed a shear thinning behaviour. The zero shear viscosity property of the fat replacers was translated into the initial resistance to deformation exhibited by the reduced-fat emulsions they were incorporated into respectively (Chapter 3.2). Reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid fat replacer had lower consistency coefficient, firmness and hysteresis compared to the reduced-fat mayonnaise-type emulsions containing starch/monoglyceride fat replacer (Chapter 3.2).

Single amylose chains have a unique ability to form complexes with a variety of complexing agents such as fatty acids, emulsifiers, and smaller ligands, such as alcohols or flavour (Le Bail *et al*., 2005). Figure 4.2 shows the formation of amylose-lipid complexes present in the fat replacer during the wet heat processing of maize starch in the presence of the lipids (stearic acid and monoglyceride) at high temperatures (>90°C) for an extended period (Nelles *et al.*, 2000; D'Silva *et al*., 2011; Wokadala *et al*., 2012). The presence of the lipids induced the formation of a compact helical conformation of amylose, displaying the V-type diffraction pattern (Putseys *et al*., 2010). The hydrophobic aliphatic fatty acid chain of the lipids goes to reside inside the rich hydrophobic inner channel of the V-amylose that is lined with methylene groups and glycosidic linkages (López *et al*., 2012; Obiro, Sinha Ray & Emmambux, 2012; Chao *et al*., 2018). Inside the cavity, the amylose-lipid interactions are stabilised by molecular hydrogen bonds and van der Waals forces between the amylose glucose residues, water molecules and the lipid (Nimz *et al.*, 2004).

The formation of amylose-lipid complexes limits the formation of junction zones, thus reducing starch gel rigidity (firmness) and consequently a resultant non-gelling paste. Available amylose molecules, after starch pasting without the addition of lipid (fatty acids and monoglycerides), associate with each other to form junction zones through hydrogen bonds (BeMiller & Whistler, 2009; Saha & Bhattacharya, 2010). This causes the starch paste to form a stable gel through molecular entanglement (Figure 4.4). Co-crystallisation of amylose with other compounds reduces the ability of amylose to form double helices that are characteristic of retrograded starch. Also, the presence of amylose-lipid complex can interfere with amylopectin re-crystallisation (Nelles *et al.*, 2000), thus retarding retrogradation. The complex formation between amylose and the lipids increase the viscosity of resultant pastes (Nelles *et al.*, 2000; D'Silva *et al.*, 2011; Wokadala *et al.*, 2012), contributing to the high viscosity and zero shear viscosities of the fat replacers.

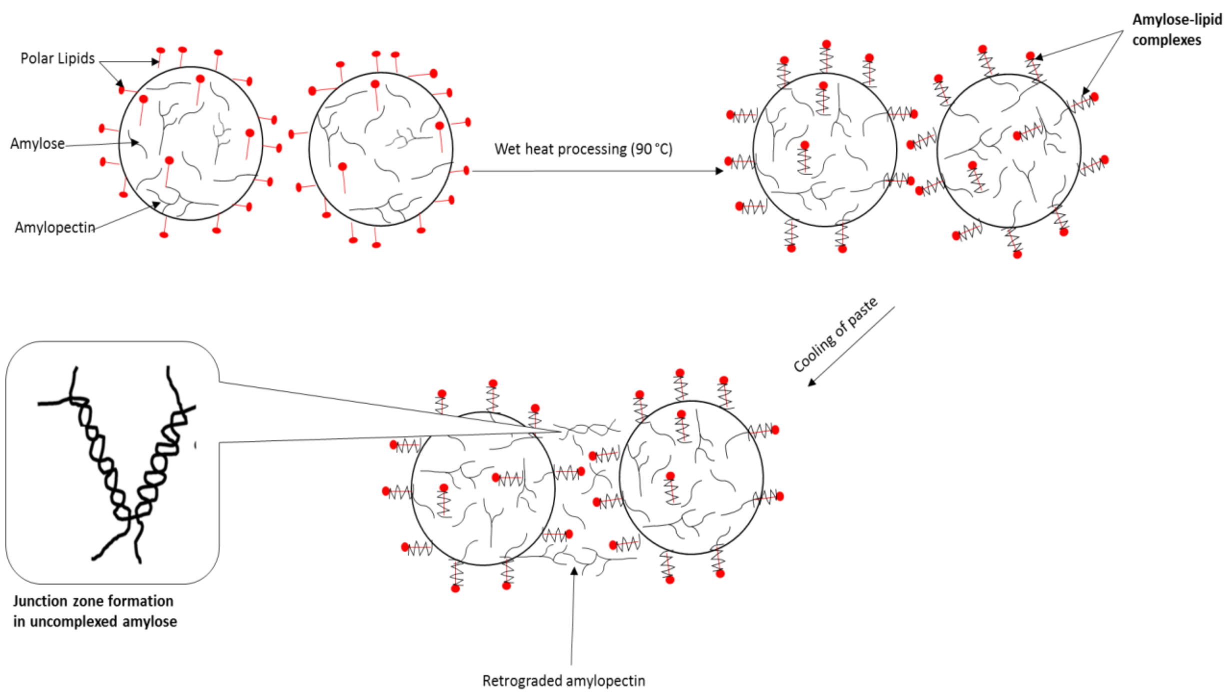

Figure 4.4. Schematic diagram showing the formation of amylose-lipid complexes between amylose and the lipids present in the paste during wet heat processing

4.2.2 Lower friction coefficient of fat replacers and reduced-fat mayonnaise-type emulsions

The fat replacers showed good lubricating properties at the boundary and mixed lubrication regime (Chapter 3.1). With the maize starch modified with 2 % monoglyceride showing lower friction coefficient at the mixed regime compared to maize starch modified with 1.5 % stearic acid. The fat replacers, when incorporated into the reduced-fat mayonnaise-type emulsions, mainly showed mixed lubrication and elastohydrodynamic lubrication regimes. In the mixed regime, reduced-fat mayonnaise-type emulsions containing starch/stearic acid had similar friction coefficient as the full-fat. On the other hand, in the hydrodynamic regime, the friction coefficient values for the starch/stearic acid emulsions were higher than those obtained for the full-fat emulsion (Chapter 3.2). In the case of the reduced-fat mayonnaise-type emulsions formulated with the starch/monoglyceride fat replacer, the friction coefficient was lower compared to the full-fat in the mixed regime. The friction coefficient was similarly low as that measured for the full-fat emulsion in the hydrodynamic regime (Chapter 3.2).

The good lubricating properties of both fat replacers were evident in the lubricity of their respective emulsions at the different lubrication regimes similar to that of the full-fat emulsion. The initial presence of oil in the reduced-fat mayonnaise-type emulsion in the form of emulsified droplets, although in small amount especially in the case of 98 % oil replacement, possibly formed a thin film in the contact area after surface-induced droplet coalescence at the polydimethylsiloxane surfaces. This possibly lubricated the contact surfaces hence reducing the friction coefficient. Dresselhuis *et al.* (2007), reported similar coalescence for emulsions with as little as 1 % oil content.

The differences in lubrication behaviour of reduced-fat mayonnaise-type emulsions formulated with starch/stearic acid and reduced-fat mayonnaise-type emulsion with starch/monoglyceride can possibly be due to differences in the ability of the emulsions to either promote or prevent oil droplet coalescence. Therefore, the higher friction in the case of reduced-fat mayonnaise-type emulsions with starch/stearic acid can be attributed to incomplete coverage of the polydimethlysiloxane substrates with oil films. And this is possibly due to the higher stability of the oil droplets present in the starch/stearic acid emulsion. Emulsions that are more sensitive to coalescence give rise to lower friction (Dresselhuis *et al.*, 2008).

It is also hypotheses that, the presence of amylose-lipid complexes that can occur as nanoparticles in the fat replacers, possibly have a nanofiller effect that will provide the emulsions with similar lubricating behaviour as the full-fat emulsion. Amylose-lipid complexes have been suggested to be at the nanoscale of less than 100 nm (Zabar *et al*., 2009; Cuthbert *et al*., 2017). The possible morphology of the V-amylose complexes as a lamellar with alternating crystalline and amorphous layers was demonstrated by Biais *et al*. (2006), with a folding length and spheroids in nanoscale dimensions (Godet, Bouchet, Colonna, Gallant & Buleon, 1996). Biais *et al.* (2006) further reported that the ligand could be positioned in three possible locations; within the helices, between the helices of the crystalline regions or dispersed in the amorphous regions. Nanostructures of amylose-lipid complexes, consisting of randomly oriented finite regions that are made up of alternating layers of crystalline and amorphous material were confirmed using small-angle X-ray scattering systems (SAXS) (Zabar *et al*., 2009; Zabar, Lesmes, Katz, Shimoni & Bianco-Peled, 2010). Cuthbert *et al.* (2017), isolated and characterised amylose-lipid complexes formed during extended pasting of maize and teff starches with stearic acid. They reported nanoparticle sizes of about 2.4–6.7 nm and 3–10 nm for maize and teff respectively.

It can, therefore, be suggested that, like protein-based fat mimetics produced through microparticulation of egg, milk or whey proteins (Akoh, 1998), the nanoparticles of the fat replacers were too small to be perceived as individual rough particles in the mouth. Instead, they were perceived to have fat-like properties (creamy and smooth texture) in the mouth that aided lubrication. Also, increase in volume to surface area ratio of the complexes possibly made them more available to act as a layer of lubricant to provide an effective barrier to reduce asperity between the tribo-surfaces, hence lowering the friction coefficient.

4.2.3 Sensory characteristics of reduced-fat mayonnaise-type emulsions in relation to rheological and tribological measurements

During oral processing, fat droplets have a great influence on the perceived texture of a product when it first enters the mouth; the food interacts with the surfaces of the oral cavity, coating of oral surfaces, and flavour release (Stokes, Boehm & Baier, 2013). The fat droplets may remain as individual entities, flocculate, or coalesce and influence texture, lubrication, and coating within the mouth (van Aken, 2010). In full-fat emulsions, fat droplets coat the oral cavity after swallowing, and this contributes to the desired flavour profile and mouthfeel. The fat droplets may also bind with flavour molecules and increase the residence time of flavour compounds to give a prolonged flavour profile perception (Doyen *et al.*, 2001; Malone, Appelqvist & Norton, 2003a). However, in reduced-fat versions, when fat droplets are removed and replaced with non-fat molecules or particles, these desirable mouthfeel attributes may be lost.

Findings from this study postulate that, during oral processing of the reduced-fat mayonnaise-type emulsions, the reduced oil mayonnaise type emulsions are mixed with saliva and exposed to biopolymers such as mucins and salivary enzymes (Sarkar, Goh & Singh, 2009). The emulsions also undergo some amount of shearing in the oral cavity. The saliva-food interaction causes a breakdown and destabilisation of the microstructure of the emulsion, exposing the amylose-lipid complexes present in the continuous phase (Figure 4.5). The bulk, as well as the surface properties of the emulsions, are destabilised, resulting in a different microstructure during oral processing (Chen, 2015). Changes in the microstructure then lead to a textural experience utterly different from that of a stable emulsion, and this has significant implication on sensory perception. The shearing of the emulsion in between the mouth and the palate, as simulated in this study using tribology, cause the little residual droplets that are more susceptible to coalescence to adsorb to the oral surfaces and reduce the friction to some extent. However, due to the limited amount of droplets in the reduced-fat mayonnaise-type emulsion, there will be limited surface coverage of the coalesced droplets for effective lubrication compared to the full coverage in the case of a full-fat emulsion. The exposed amylose-lipid complexes in the fat replacers adsorb and fill-up the spaces in between droplets and thus reduce the asperity between the oral surfaces. This is influenced by the nano-particulate and adhesive nature of the amylose-lipid complexes (Cuthbert *et al.*, 2017). The complexes sustain a high viscous matrix (continuous phase) with amylose lipid nanomaterials acting as a nano-filler to ensure smooth and continuous lubrication providing a fat-like oral sensory perception.

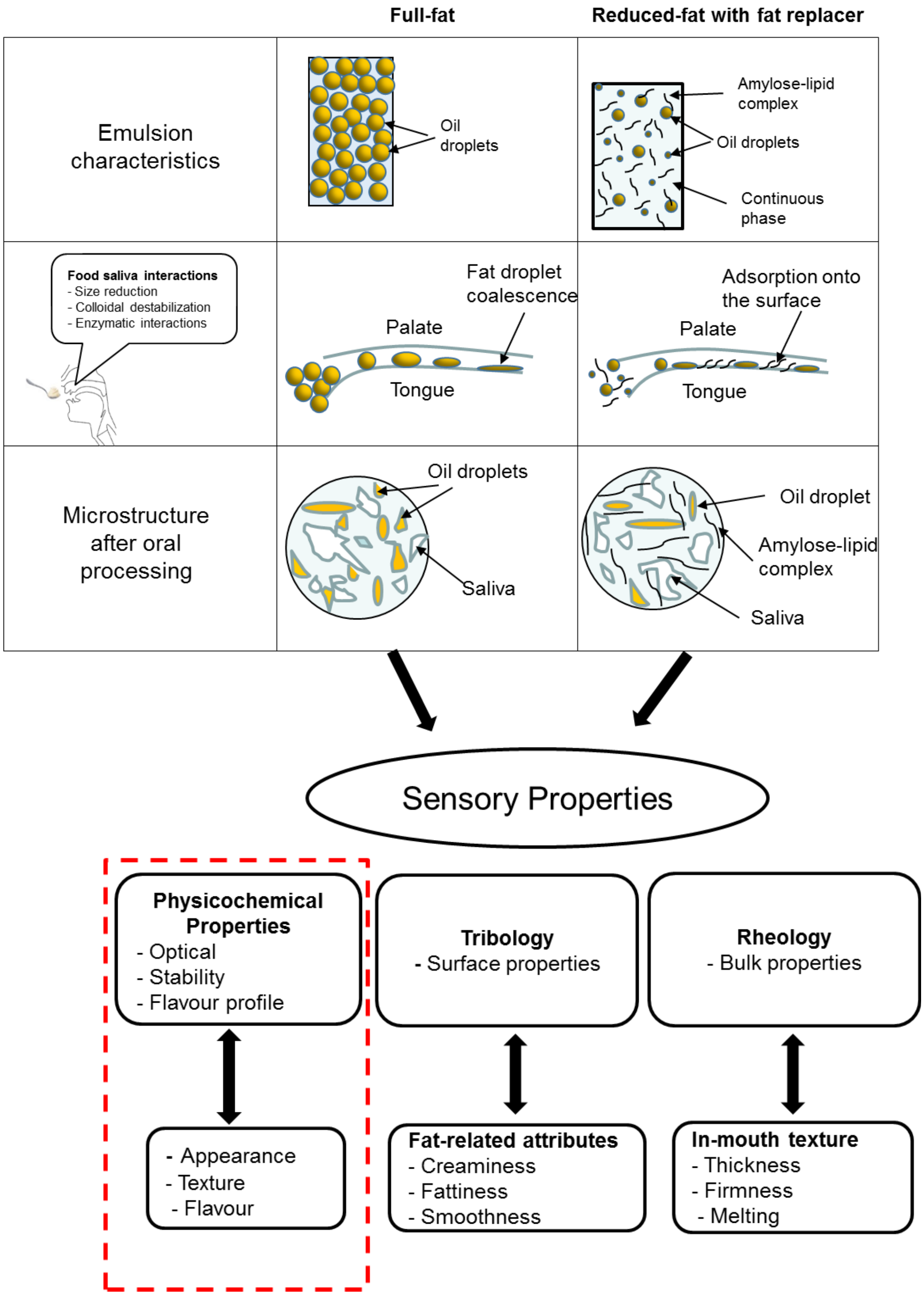

Figure 4.5. Schematic diagram representing the effect of addition of fat replacers on the microstructure of reduced-fat mayonnaise-type emulsions during oral processing and its influence on sensory perception

Food oral processing is a dynamic process where the relation between textural properties and sensory perception can be described using the changing length-scale of an eating process (Chen & Stokes, 2012) when the sensory perception of the emulsion is perceived consistently and integrated throughout the whole eating sequence (Figure 4.6). Food emulsions exhibit a range of textural characteristics (low-viscosity fluids, high-viscosity fluids, viscoelastic solids and solids) depending on their composition, structure, and interactions (McClements, 2015). All the reduced-fat mayonnaise-type emulsions can be classified as being viscoelastic solids. Fat droplets contribute greatly to these textural characteristics; however, non-fat ingredients such as hydrocolloids, starch granules also have an effect on the texture of emulsions they occupy the continuous phase. Emulsions are ingested as a big lump and gradually thin out due to shearing and mixing with saliva.

The fat replacers and all the reduced-fat mayonnaise-type emulsions exhibited a shearing thinning behaviour with an initial zero shear viscosity. These bulk properties correlated with the sensory properties thickness, melting, and ease-to-swallow. The reduced-fat mayonnaise-type emulsion formulated with starch/stearic acid fat replacer that had lower zero shear viscosity, firmness and hysteresis compared to the starch/monoglycerides emulsions, and the latter were associated with being melting and easy to swallow. While the reduced-fat mayonnaise-type emulsion formulated with starch/monoglycerides fat replacer were perceived more as being thick. Texture perception of emulsions is a highly dynamic process and changes continuously during oral processing. Different sensory attributes are perceived during different stages of mastication; hence, a temporal dominance sensation method could also be employed to measure the intensity of dominant textural attribute throughout the eating process.

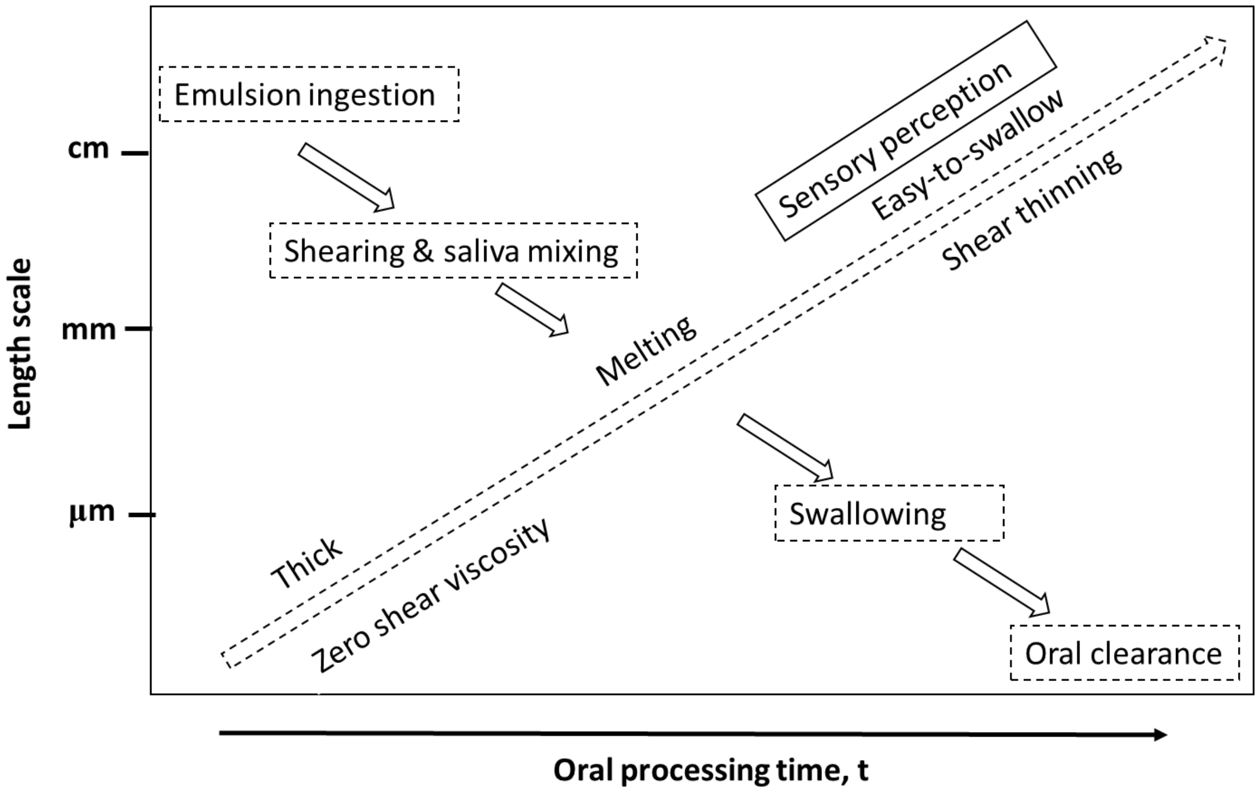

Figure 4.6. Decreasing length-scale of reduced-fat **mayonnaise-type** emulsions and oral surface contacts from the first ingestion till oral clearance. Continuous dynamic sensory perception indicated by dashed arrow

Adapted from (Chen & Stokes, 2012)

Emulsions are subjected to colloidal destabilisation that alters its microstructure when ingested. Salt induced aggregation, depletion flocculation, bridging flocculation, and coalescence (Chen, 2015) are the four possible oral destabilisations that can occur in food emulsions as a result of saliva mixing and oral shearing (Sarkar & Singh, 2012; Chen, 2015). However, depletion flocculation and bridging flocculation are the most likely mechanisms, especially in reduced-fat emulsions (Dickinson, Hunt & Horne, 1992).

Mucin, a major protein component in saliva, play an essential role in the flocculation of emulsions because of their negative charge at neutral pH (van Aken *et al*., 2005; Silletti *et al.*, 2007). Also, the charge status of the droplets in an emulsion is critical for their oral stability (Silletti *et al.*, 2007). Strongly negatively charged emulsions will normally remain stable due to repulsive forces that prevent emulsion droplets from sticking together. On the other hand, positively charged emulsions are easily destabilised due to flocculation caused by simultaneous absorption of mucins and other abundant salivary proteins to the surface of the positively charged emulsion droplets (Chen, 2015). Modification of starches increases their surface activity (Magnusson & Nilsson, 2011) and the presence of the glycosyl hydroxyl groups located on the surface of the starch-lipid complex can make the fat replacers negatively charged (Magnusson & Nilsson, 2011; Seo, Kim & Lim, 2016). Based on the above considerations and the high stability of the emulsions observed during the tribology measurements (Chapter 3.2), one can assume that the reduced-fat mayonnaise-type emulsions were negatively charged. Also, α-β-livetin, the water-soluble protein of egg yolk, is expected to have a net positive charge at low pH (Nilsson, Osmark, Fernandez, Andersson & Bergenståhl, 2006). Therefore, the modified starches may adsorb to the α-β-livetin-coated interface and give rise to a thicker interfacial layer, possibly increasing the stability of the reduced-fat mayonnaise-type emulsions. The charged status of the emulsions can, however, be determined by measuring the Zeta (ζ) potential using an Electroacoustic Spectrometer in future studies.

A stable emulsion would typically be perceived as smooth and creamy, but a flocculated emulsion would often be sensed as rough and dry with probably increased thickness sensation (Vingerhoeds *et al.*, 2009). Results from this study showed that both fat replacers were glossy in appearance, and had a creamy and smooth texture (chapter 3.1). When incorporated into the production of the reduced-fat mayonnaise-type emulsions, all the reduced-fat emulsions were rated high for smoothness, melting, and easy-to-swallow (chapter 3.2). Also, the thickness, creaminess and mouth-coating ratings for all the reduced-fat emulsions formulated with starch/monoglyceride were similar to that of the full-fat mayonnaise emulsion. These findings, therefore, indicate the possible absence of flocculated droplets. In a full-fat oil-in-water emulsion, containing only fat droplets dispersed in water, viscosity increase with increasing fat content (McClements, 2015). In reduced-fat emulsions where fat droplets are removed, there is a decrease in viscosity, which may result in a conversion of the soft gel-like structure of the emulsion into a fluid product (McClements, 2015). For instance, mayonnaise may lose its thickness and spoonability when the fat droplet content is reduced below a certain level. Modifying the continuous phase with the addition of the fat replacers resulted in a microstructure with smaller oil droplets compared to the full-fat. This provided the reduced-fat mayonnaise-type emulsions with similar lubricating properties as the full-fat contributing to the perceived smoothness and creaminess mouthfeel. Moreover, the reduced-fat emulsions were more like a soft gel due to the lipid-modified starches as a fat replacer.

The inconsistencies observed in the consumer feedback affected the quality of the consumer data hence making it difficult to make definite decision on the data. However, from the data, a predicted trend was observed. The reduced-fat mayonnaise-type emulsion with quality properties such as smoothness, creaminess, good lubricity and shelf-stability similar to the commercial references was most preferred, that is the reduced-fat mayonnaise-type emulsion formulated by substituting 80 % of sunflower oil with starch/monoglyceride. This suggests that the addition of the lipid-modified starches successfully modified the microstructure of the emulsions by mimicking the properties of fat, especially in aspects of in-mouth textural properties and lubrication. However, concerning the commercial viability of the reduced-fat mayonnaise-type emulsions, further research into the oxidative stability of the reduced-fat mayonnaise-type emulsions is recommended. This is because, the predictive real-time storage days based on the calculated accelerated shelf life (Chapter 3.3), will be way below the expected storage days (6 - 12 months) for mayonnaise (McClements & Demetriades, 1998; Sainsbury et al., 2016).

Flavour perception during food consumption is determined by the nature and amount of volatile and nonvolatile compounds (Overbosch *et al.*, 1991). During the complex oral processing of emulsions, flavour compounds are progressively released from the food matrix. This phenomenon is dependent on the food texture, the composition as well as in-mouth breakdown. The fat replacers had a less intense aroma and flavour, which was proposed to be a positive attribute since it would have no adverse effect on products there are incorporated into. However, the descriptive panel rated all the reduced-fat mayonnaise-type emulsions generally low for overall flavour compared to the commercial references. Also, from the consumer rejection comments, it can be suggested that the flavour of the reduced-fat emulsions were not comparable to the commercial references. It must, however, be stated that the commercial mayonnaise references contain acid regulators, and flavourings to improve their overall flavour intensity. All the reduced-fat mayonnaise-type emulsions did not contain acid regulators and flavourings. Nevertheless, this study could not fully establish the relation in changes of the microstructure of the reduced-fat mayonnaise-type emulsions during oral processing on the physicochemical properties such as optical and flavour profile. This is highlighted with dashed-red lines in figure

4.4 above and further research is recommended. Addition of acid regulators and flavourings could improve the overall flavour intensity of the reduced-fat mayonnaise-type emulsions to meet consumer expectation. Mayonnaise derives the characteristic flavour from isothiocyanates, present in mustard used as an ingredient in the formulation (Depree & Savage, 2001). In food emulsions, flavour molecules partition between the oil and aqueous phases depending on their relative solubility (Chung & McClements, 2014). Isothiocyanates react with water and OH^{-} ions in aqueous solutions but with the addition of citric acid, the rate of the breakdown is retarded, and isothiocyanate becomes more stable (Depree & Savage, 2001).

The relation between flavour release and perception is complex and influenced by several factors. These include, the rate of release of aroma and taste compounds from the food; properties of the food such as composition and texture; and the overall integration of the sensation induced by the food consumption (aroma, taste, texture, temperature, etc.) (Cook, Hollowood, Linforth & Taylor, 2003; Hort & Hollowood, 2004; Salles, Chagnon, Feron, Guichard, Laboure, Morzel, Semon, Tarrega & Yven, 2010). Saliva-food matrix interaction also influences the profiles of flavour compounds that are released, affecting consumer perception (Salles *et al.*, 2010). Thus, the physiological parameters, as well as modification of the food properties, can affect the overall flavour perception. Addition of the fat replacers apart from giving viscosity to the reduced-fat mayonnaise-type emulsions, therefore, possibly retarded the release of aroma and taste compounds hence affecting the overall flavour intensity.

Several studies have proposed the use of starch-lipid complexes as food additives in low-fat foods for their desirable functionalities and properties (Singh & Byars, 2009; Singh & Kim, 2009; D'Silva *et al.*, 2011; Maphalla & Emmambux, 2016; Cuthbert *et al.*, 2017). Teklehaimanot *et al.* (2013) investigated the potential of these complexes (maize and teff starches modified with 1.5 % stearic acid) as fat replacer after incorporating them into the production of low-calorie mayonnaise type emulsions. In the study, it was found that replacing sunflower oil at 50 % and 80 % with the lipid-modified starches produced low-calorie mayonnaise-type emulsions (76 % lower calorific value) with higher viscosity and smaller oil droplets compared to full-fat mayonnaise. All the samples were stable to freeze-thaw cycles and high-temperature during a storage period of 28 days. However, in these investigations, the tribological and sensory properties of these complexes on their own, as food ingredients providing specific product properties were not researched.

This study, apart from characterising (tribological, rheological and sensory profile) starch-lipid complexes as fat replacers, it has also established the tribological, rheological and sensory profile of their respective reduced-fat mayonnaise-type emulsions. Findings from this study suggest that viscosity differences did not effectively discriminate the differences in the oil replacement levels (50, 80 and 98 %), but rather had a link to flavour intensity. The rheological measurement mainly predicted the thickness sensory perception of the emulsions. However, tribology measurements showed similar trends as the sensory results in discriminating between the different oil replacement levels. The tribological measurements correlated with fat-related sensory perceptions such as creaminess, smoothness, oiliness and mouth-coating. This is mainly due to the colloidal principles that explain the oral processing of emulsions. The results of this study suggest that tribology measurements are more related to sensory perception. The research findings also suggest that tribology data (friction coefficient) could be used as instrumental parameters related to fat perception, whereas viscosity is less sensitive.

However, several types of research have come to a consensus on the transformation during oral processing from rheology to tribology (Chen & Stokes, 2012; Prakash, Tan & Chen, 2013; Stokes *et al*., 2013; Pradal & Stokes, 2016; Sarkar, Kanti, Gulotta, Murray & Zhang, 2017). They hypothesised that the textural features sensed at early stages of oral processing are those mostly dominated by bulk phase properties (i.e., rheology). In contrast, those sensed at a later stage of oral processing are related to thin-film properties of a product and/or product-saliva combination (i.e., oral tribology). This is explained by Chen and Stokes (2012) based on the Kokini’s model of oral lubrication (Figure 4.7), where the given sensory properties show the varying contribution of oral lubrication and food rheology, highlighting a transition between the two regimes. Therefore, a comprehensive determination of rheological and tribological properties will complement each other in the understanding of texture and mouthfeel sensory perception of reduced-fat mayonnaise-type emulsions.

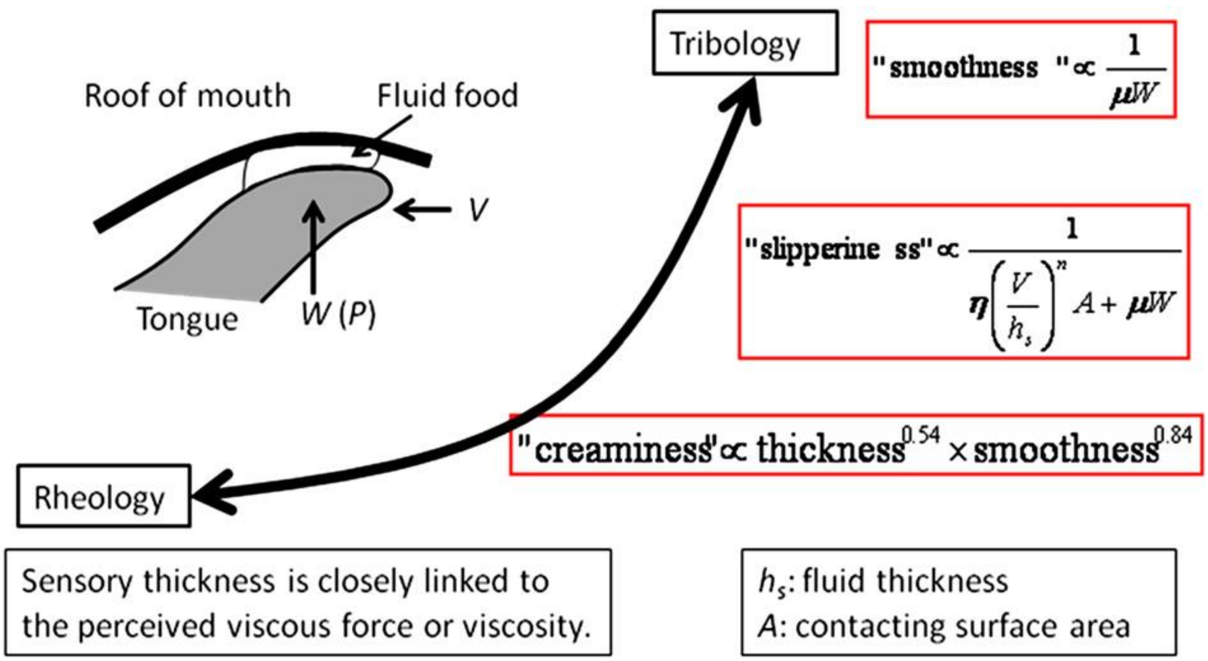

Figure 4.7. A diagram showing the varying contribution of oral lubrication and food rheology to sensory properties based on Kokini's model of oral lubrication. Where *h* is the viscosity, *V* is the speed of tongue movement, *W* is the surface load, μ is the friction coefficient

(Chen & Stokes, 2012)

In this study, only the viscosity and related measures of the reduced-fat mayonnaise-type emulsions were considered. Other equally important rheological properties such as viscoelasticity and phase transition of the emulsions were not researched. Several researchers have reported a relationship between viscoelasticity and emulsion stability (Murray & Ettelaie, 2004; Damodaran, 2005; Brugger, Rosen & Richtering, 2008; Dickinson, 2010). Therefore, small-deformation viscoelasticity properties of the reduced-fat mayonnaise-type emulsions at the different oil replacement levels (50, 80 and 98 %) can be investigated using a dynamic oscillatory rheometry. This could provide additional information on the structure and shelf-stability of the emulsions. Different physical forces such as density difference between the dispersed and the continuous phases and inter-particle interactions between droplets affect the kinetic stability (creaming, flocculation/aggregation, and coalescence) of emulsion droplets during storage (Damodaran, 2005).

The different storage and utilisation temperatures of foods cause emulsified fats to crystallise (Sato, 1999), and semi-crystalline droplets are usually less stable (Vanapalli & Coupland, 2001). This, therefore, makes it important also to investigate the possible phase transition (fat crystallisation) that could occur in the reduced-fat mayonnaise-type emulsions during storage. Ultrasonic velocimetry technique, recommended by Singh, McClements and Marangoni (2002), can be used to measure the temperature dependence crystallisation in the reduced-fat mayonnaise-type emulsions.

4.3 CONCLUSIONS, RECOMMENDATION AND FUTURE PERSPECTIVE

Wet-heat processing of maize starch and lipids (stearic acid and monoglycerides) produces starch-lipid complexes that can be used as fat replacer because they have properties such as being glossy, creamy, smooth, and transparent with mouth-coating properties similar to oil, which gives them good lubricity. The lipid-modified starches are paste-like, non-gelling, and contain amylose-lipid complexes. Thus the lipid-modified starches exhibit fat-like properties and show great potential as fat replacers, for producing non-gelling emulsions with a creamy and smooth texture.

Lipid-modified maize starches can successfully replace fat up to 80 % in emulsion to substitute sunflower oil. The lipid-modified starches as fat replacers produce reduced-fat mayonnaise-type emulsions with good tribological and in-mouth textural attributes such as creaminess, smoothness, oiliness, mouth-coating, and are as easy-to-swallow comparable to full-fat mayonnaise. The amylose-lipid complexes present in the fat replacers possibly have a nano-filler effect that provides the emulsions with a non-gelling high viscous matrix, stabilise residual oil droplets, and also enable oil-droplet coalescence at the interfaces for good lubrication.

The addition of lipid-modified starches in the formulation of the reduced-fat emulsions does not effectively retard the rate of lipid oxidation in the reduced-fat mayonnaise-type emulsions at accelerated storage. Increased rate of lipid oxidation can be due to the presence of liberated iron ions, Fe^{2+}, from the egg yolk present in the aqueous phase. The available Fe^{2+} possibly initiated and accelerated the rate of oxidative rancidity in the reduced-fat mayonnaise-type emulsions. Starch/monoglyceride fat replacers produce the most acceptable reduced-fat mayonnaise-type emulsions with up to 80 % sunflower oil replacement. Starch/monoglyceride emulsions have accelerated shelf-life beyond 35 storage days.

To further understand the rheology and sensory relationship, it is recommended that additional rheological measurements (viscoelasticity and phase transition) and further research in the area of optimising the appearance and flavour of the emulsions to meet consumer expectation is recommended. The research data will complement findings from this study to produce sustainable reduced-fat mayonnaise-type emulsions with sensory characteristics similar to the full-fat counterpart that would have greater acceptably.

It is also recommended that tribological measurements of the reduced-fat mayonnaise-type emulsions should investigate the addition of artificial saliva. Although, the amylose-lipid complexes present in the fat replacers are classified as resistant starch and may not be susceptible to alpha-amylase present in the mouth, the effect on amylopectin needs consideration. The inclusion of saliva in any eating process is inevitable. This will help mimic the actual oral processing of reduced-fat mayonnaise-type emulsions and give a better understanding of the role of saliva on the viscosity and lubricity of the emulsions, and their effect on sensory perception.

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PUBLICATION, PRESENTATIONS AND POSTERS FROM THIS RESEARCH

Publication(s)

Agyei-Amponsah J., Macakova L., DeKock H.L., and Emmambux M.N., 2019. Sensory, tribological, and rheological profiling of "clean label" starch–lipid complexes as fat replacers. *Starch-Stärke*, 71, 1800340.

Conference oral presentation

Agyei-Amponsah J., Macakova L., DeKock H.L., and Emmambux M.N., Rheology, tribology and mouthfeel sensory profiling of mayonnaise-type emulsions formulated using 'clean label' fat replacers. 23rd Biennial International SAAFoST Conference & exhibition, 1-4th September, 2019, Johannesburg, South Africa.

Agyei-Amponsah J., Macakova L., DeKock H.L., and Emmambux M.N., Sensory profile, tribology and rheology of maize starch modified with stearic acid and monoglyceride. 19th IUFoST World Congress of Food Science and Technology, 23rd -27th October, 2018, Mumbai, India.

Conference poster

Agyei-Amponsah J., Macakova L., DeKock H.L., and Emmambux M.N., Mouthfeel sensory profiling, rheology and tribology of mayonnaise-type emulsions formulated using 'clean label' fat replacers. 13th Pangborn Sensory Science Symposium, 28 July - 1 August, 2019, Edinburgh, UK

Agyei-Amponsah J., Macakova L., DeKock H.L., and Emmambux M.N., Tribology, rheology, texture and sensory profile of fat replacers for emulsions. 5th International Conference on Food Oral Processing. 1st – 4th July, 2018, Nottingham, UK

Agyei-Amponsah J., Macakova L., DeKock H.L., and Emmambux M.N., Tribology, rheology, texture and sensory profile of fat replacers for emulsions. 22nd Biennial International SAAFoST Congress & Exhibition, 3rd - 6th September, 2017, Cape Town, South Africa.

Appendix 1. Training for recruiters

BRIEF ON THE PROJECT

This research is aimed at finding a dietary alternative to help address the issue of obesity and its related illnesses.

In this research mayonnaise samples, are produced from food ingredients that are safe to humans and the environment.

This product, if successful, could contribute to the wellbeing of the society and also help people adapt and maintain a low-fat diet.

LEARNING OUTCOME

- Know the right consumer - Target group
- Responsibilities of a recruiter
- Responsibilities of the consumer
- Recruiting techniques (Dry run)
- How to terminate an interview

TARGET POPULATION (CONSUMER)

- The most important aspect in selecting suitable persons for these tests is to make sure that they are **representative of the target consumer group** (consumers should consume mayonnaise at least once a week)

- The consumers should be **naïve** and **do not require any training** with regard to sensory evaluation in general or **the specific attributes of a product**.

- The **number of consumers** to recruit will depend on the design of the experiment. It is advisable to recruit a suitable percentage of consumers more than the requirement to allow for non-arrivals or non-completers.

- A representative mixture (i.e. male, females, blacks, whites, foreigners etc…) should as much as possible be used.

- Persons that have been trained for descriptive sensory evaluation tasks should preferably not be used for consumer evaluation tasks.

- Individuals that have technical or related information about the product samples under investigation will also not represent the naïve target market for consumer sensory evaluation.

RESPONSIBILITIES OF A RECRUITER

Dos

- As a field worker (recruiter), you will be required to recruit 16 persons for a particular day and time slot.

- Attendance of the people you recruit to the sensory session at their specified date and time will be your responsibility.

Don'ts

- Do not give too much information to the consumers

FOR THE CONSUMER

- As a consumer, you play a vital role in product development.

- Participants will attend a 30 min tasting session in the sensory laboratory on the University of Pretoria campus. Specify date and time to the consumer.

- During the session, participants will have to taste and evaluate 12 small portions of mayonnaise

- As an incentive, each participant will receive a gift voucher worth R 25.

HOW TO TERMINATE AN INTERVIEW?

E.g. "thank you very much for your time. Unfortunately, you are not the kind of person for this research". Thank you.

Training

- Go through the questionnaire
- Conduct a dry run
- Discuss day and time allocation

Appendix 2. Screening questionnaire

Dept of Consumer and Food Sciences

Dear Sir/Madam

The Consumer and Food Sciences Department of the University of Pretoria is conducting research aimed at develop food products to address obesity and its related illnesses.

In this research low-fat mayonnaise is produced from ingredients that are better for humans and the environment. This product, if successful, could contribute to the wellbeing and also help people adapt and maintain a low-fat diet. As a consumer, you play a vital role in product development. Your opinion about the taste of the mayonnaise is of interest in this research.

Participants need to attend a 30 min session in the sensory laboratory on the University of Pretoria campus. During the session, participants will have to taste and evaluate 12 small portions of mayonnaise. As an incentive, each participant will receive a gift voucher worth R25.

The date and time of the session is:

Date:	Time:

Are you interested and willing to participate?

Recruitment agent name and contact details:	

Yours faithfully,

Joyce Agyei-Amponsah

(PhD student)

Mrs Joyce Agyei-Amponsah is a PhD student in the Dept of Consumer & Food Sciences under the supervision of Prof N M Emmambux and Prof H L de Kock. Ethical approval for this study has been granted by the Faculty of Natural & Agricultural Sciences, University of Pretoria EC 170425-111

Screening questionnaire

The research seeks participants that meet certain criteria. To find out if you are one of the participants being sought, I need to ask you a few questions.

1. On average, how many times per week do you consume mayonnaise? *Listen to the answer*

At least once a week	***Continue***
If less that once a week or do not consume mayonnaise	***Terminate interview***

2. Are you allergic to any food/food ingredients?

No	***Continue***
Yes	***Terminate interview***

3. The product that you will be asked to taste may contain (Sunflower o*il, egg, vinegar, salt, sugar mustard, modified starch and preservatives*). Are you willing to taste the products?

Yes	***Continue***
No	***Terminate interview***

Thank you, you meet the criteria for the research. I would like to remind you about the session and for this I need your name, and contact details. This information will be treated confidentially by the researchers.

Name	
Email	
Phone No.	

Interviewer section: I ……………………………………………………….……………. (Full name & surname) hereby declare that I have screened the respondent and that the above information is correct and valid to the best of my knowledge.

Signature: ……………………….. **Date: ……………………………**

Contact number	
Student number	

Appendix 3. Consent form

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Dept of Consumer and Food Sciences

Consent form: Consumer evaluation of mayonnaise type emulsions formulated with different fat replacers – May 2018

Joyce Agyei-Amponsah is a PhD student in the Dept of Consumer & Food Sciences. Her research focuses on developing low-fat mayonnaise to address obesity and its related illnesses.

What will you be asked to do?: You will be required to taste and evaluate 12 small portions of mayonnaise.
How long will it take?: Evaluation of the samples is expected to be completed within 30 min.
Why should you participate?: As a consumer, you play a vital role in product development and your opinion about the taste of the test mayonnaise is very important. This product, if successful, could contribute to health and wellbeing of consumers. As a token of appreciation for your time and effort, you will receive a R25 gift voucher.
Are there any risks?: The mayonnaise samples were produced with legally approved ingredients for use in food products. The products may contain: sunflower oil, egg, modified starch, vinegar, sugar, salt, mustard, and preservatives: sodium benzoate and potassium sorbate. The only risk may be the energy intake associated with consumption of the mayonnaise samples. You will be asked to taste small quantities per sample (2 ml) and expectorate the samples if need be.
Disclaimer: Note that participation is voluntary and at your own risk. The University of Pretoria, nor any of its representatives, can be held responsible in the unlikely event of any injury or illness as a direct or indirect result of your participation in this tasting session.
What will you do with my answers?: The answers you give will be used for research purposes only and to make decisions about the products. Your identity will not be linked to your responses.
Do you have to participate?: You do not have to participate in this research project. Your participation is completely voluntary and you may decide to opt out. You can stop participating at any time without penalty.

If you have any questions about the research, please ask one of the assistants or contact the project supervisor Prof. Riette De Kock – Tel: 021 -420 3238

I HAD THE OPPORTUNITY TO READ THIS CONSENT FORM, ASK QUESTIONS ABOUT THE TASK AND I VOLUNTEER TO PARTICIPATE.

____

Signature of participant Date:

____

Name of the participant (print clearly)

HLdeKock

____

Signature of project coordinator (Prof. H.L. deKock) PhD student (Ms Joyce Agyei-Amponsah