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FORMATION OF LOW DENSITY AND FREE-FLOWING HOLLOW MICROPARTICLES FROM NON-HYDROGENATED OILS AND PREPARATION OF PASTRIES WITH SHORTENING FAT COMPOSED OF THE MICROPARTICLES

By

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FORMATION OF LOW DENSITY AND FREE-FLOWING HOLLOW MICROPARTICLES FROM NON-HYDROGENATED OILS AND PREPARATION OF PASTRIES WITH SHORTENING FAT COMPOSED OF THE MICROPARTICLES

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University of Nebraska, 2019

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Solid fats provide critical functionality in the structuring, shortening, and stabilizing of many foods. However, their use as an ingredient is foods can present a number of challenges. The physical properties of solid fat can make them difficult to apply to or incorporate into foods consistently. On an industrial food production scale, handling of solid fats can difficult because they are often packed in heavy cubes or totes, and production delays and inefficiencies may be caused by the need to remelt the oils before use. Oils as a macronutrient also contribute a relatively high number of calories at 9 calories per gram.

The overall objective of this thesis is to create micron size hollow solid fat particles using supercritical CO_2 that are free-flowing, easy to handle, quick to remelt, and simple to incorporate into foods. Specific objectives include forming free-flowing hollow solid lipid microparticles from fractionated palm oil and low moisture butter using CO_2, to characterize these novel lipid particles, and to test the performance of these particles as a shortening in pastry products.

The solid fat particles produced were composed using 50:50, 25:75, and 0:100 ratios of butter and fractionated palm oil respectively. In presence of 120 bar pressurized CO_2, the melting point of the fractionated palm oil decreased from 66.2 to 47.3 °C. The density of the particles decreased 5 folds compared to that of the original oils. With increasing fractionated palm oil

content, the particle size decreased. Ten percent ($d_{10\%}$) and fifty percent ($d_{50\%}$) of the 100% palm oil particles were smaller than 4.49 µm and 23.0 µm, respectively, whereas they were 14.5 µm and 58.3 µm when mixed with butter at 50% butter concentration, respectively. The hollow structure was more pronounced for the particles obtained from higher melting oils/oil blends, as well as with more spherical uniformity.

When used as the shortening fat in pastries, the microparticles increased firmness and thickness. Their high ratio of surface area to mass does hold potential for other applications, and the small size and free-flowing nature did make the particles easy to mix into the pastry flour.

The micron size hollow particle format for solid fats has the potential to provide a number of important benefits. It could allow for reduced calorie contributions from fat, better finished product quality, improved solid fat handling, and easier fat incorporation into formulas.

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Organization

This thesis contains five chapters and references can be found at the end of each chapter. Chapter 1 is the introduction and thesis objectives, chapter 2 contains the literature review, chapters 3 and 4 contain the two research projects, and chapter 5 contains the summary, conclusions, and recommendations. Each section has been formatted using guidelines for the *Journal of American Oil Chemists' Society*.

CHAPTER 1. INTRODUCTION AND THESIS OBJECTIVES

1.1. Introduction

Solid fats play critical roles as ingredients where they provide structuring, shortening, and stabilizing in a diverse range of foods. Foods that depend of solid fat functionality for their unique characteristics include margarines and tablespreads, baked pastries, icings and fillings, confectionaries, and some fried products. Although solid fats are required components in these foods, their use can present a number of challenges in areas that include: preparation, handling, storage, melting, incorporation into foods, and nutrition. On an industrial food production scale, solid fats like butter and shortening can cause process inefficiencies. They are often packaged and stored in cubes or large totes that can be difficult to handle. Totes of solid fats require the use of heavy equipment to transport to ingredient batching areas and usually need to be melted before incorporation into the batch (Zhou et al., 2011). Cubes of solid fat are heavy and difficult for operators to add during batching (Loughrin, 1987). After being added to a batch mixture, many production procedures will then require a time-consuming waiting step to allow the solid oil to melt so it can be uniformly dispersed into the batch. Solid fats may also be stored in large bulk tanks at production plants, but bulk tank storage requires the oil to be heated above its melting point to be pumped. The elevated temperatures required can require costly energy to maintain and may also accelerate oil degradation (Crapiste et al., 1999). On a smaller foodservice or home kitchen level, solid fat handling can also be challenging. Cold butter can be difficult to spread evenly onto bread without the presence of butter clumps or potentially tearing the bread. When preparing baked pastries, kneading butter and/or shortening uniformly into the dough can also be difficult. If the solid fat is not properly dispersed throughout the dough, the baked good will have poor finished product quality with an inconsistent and undesirable texture. A potential solution to

these challenges is to create small solid fat particles that are free-flowing, easy to handle, and simple to incorporate into foods.

The exciting role of supercritical fluid technology for particle formation has attracted interest in the recent years (Fahim et al., 2014; Lubary et al., 2011; Yang and Ciftci, 2016). Carbon dioxide (CO_2) is a preferred supercritical fluid because it has mild critical temperature and pressure (31 ºC, 74 bar), and it is nontoxic, non-flammable, environmentally friendly, inexpensive and safe. In previous studies, micron size solid lipid particles were formed using particle from gas saturated solutions (PGSS) or gas assisted melting atomization (GAMA) methods (Sampaio de Sousa et al., 2007; Mandžuka and Knez, 2008; García-González et al., 2010; Lubary et al., 2011; Bertucco et al., 2007). Recently, Yang and Ciftci (2016) reported the generation of hollow solid lipid micro- and nanoparticles from fully hydrogenated soybean oil via atomization of a CO_2-expanded solid lipid through a nozzle. In the process of Yang and Ciftci (2016), upon depressurization, the Joule-Thomson effect caused cooling at the nozzle and the surrounding area which allowed for rapid crystallization of the liquid lipid to form hollow solid lipid particles (Yang and Ciftci, 2016). For successful lipid particle formation, the lipid material must have a melting point sufficiently above the ambient temperature where the CO_2-expanded lipid is being depressurized and atomized. Although fully hydrogenated oils are suitable candidates for lipid particle formation using the method recently reported by Yang and Ciftci (2016) due their composition of mostly a single triacylglycerol (around >85% stearic acid for fully hydrogenated soybean oil) and therefore sharper melting point, a potential issue with using hydrogenated oils is that certain consumers have an aversion to seeing hydrogenated oils on a food's ingredient statement (Cargill, 2017). Nonhydrogenated oils and their blends are potential candidates to form such lipid particles but their behavior during particle formation via atomization of CO_2-expanded lipid has not been

studied due to the wide melting range of nonhydrogenated oils resulting from presence of diverse triacylglycerols. The potential benefits of forming free flowing and low-density lipid microparticles composed of non-hydrogenated oils therefore warrants further study to determine the formation feasibility, the melting behavior of the oils in pressurized CO_2, and the characteristics of the formed particles.

A potential application where the novel hollow, free-flowing lipid microparticles formed using supercritical CO_2 could provide unique benefits is in the preparation of baked pastries where solid fats are important to the finished product quality. The solid fats in pastries help to create a desirable flaky texture after baking, and this functionality is provided by interfering with the gluten matrix that forms in dough made with the flour from wheat or other cereal grains (Knightly, 1981; Baker and Mize, 1942; Baldwin et al., 1963; Harvey, 1937). These gluten proteins in the flour form the dough and give it its strength and elasticity (Hirahara and Simpson, 1961). Despite the importance of gluten in pastries, overdevelopment of gluten can create undesirable textures that are too firm or chewy. A properly shortened pastry is expected to be crumbly with a soft, flaky texture. Shortenings interrupt the formation of the gluten strands in dough leading to a "shorter", less elastic dough development (Finney et al., 1987; Souza et al., 1994; Lowe et al., 1938). Lipid microparticles formed using supercritical CO_2 could offer potential solves for the challenges of using traditional solid fat formats. The obtained hollow solid lipid microparticles are straightforward to handle and could be incorporated into pastry doughs easily. Furthermore, the small particle size and hollow nature contribute to a high ratio of surface area to mass which could allow for reduced fat usage while still functioning to interfere with the gluten matrix of the pastry. The performance of hollow solid lipid microparticles as shortening fat in baked pastries does not appear to have yet been assessed. Further study would include making a variety of baked pastries

using lipid microparticles as the shortening fat and characterizing the finished product quality of the pastries relative to traditional shortenings.

1.2 Thesis objectives

The overall objective of this thesis is to create micron size hollow solid fat particles using supercritical CO_2 that are free-flowing, easy to handle, quick to remelt, and simple to incorporate into foods. Specific objectives were:

1) To free-flowing hollow solid lipid microparticles from fractionated palm oil and low moisture butter using CO_2

2) To characterize these novel lipid particles

3) To test the performance of these particles as a shortening in pastry products.

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CHAPTER 2. LITERATURE REVIEW

2.1. The Importance and Functionality of Solid Fats in Industrial Food Applications

Solid fats are critical components of many foods and play a crucial functional role in the structuring, shortening, and stabilizing of a wide variety of foods. Key foods that use solid fats during formulation and processing include margarines and tablespreads, baked pastries, icings and filling, confectionaries, and some fried products. The importance and functionality of solid fats in each of these key foods will be explored and discussed .

2.1.1. Margarines and Tablespreads

The solid fats used in margarines and tablespreads provide important functionality in the form of plastic consistency. When stress is applied, the plastic solid fat will allow for continuous deformation without rupture, which creates the spreadable texture of the tablespread (McGraw-Hill, 2003). Ideally, the formulated oil blend should have a melting point that is below that of human body temperature to facilitate quick melting on the palate without a waxy mouthfeel (Hastert, 1990). The formulated oil blend should also have a melting point that is at least above the product's storage temperature, which is typically refrigeration temperature (4 ºC), and it may have a melting point above room temperature for improved stability during usage (Saadi et al., 2012).

Margarine contains at least 80% oil. Spreads containing less than 80% oil do not meet the standard of identity for the margarine naming convention (FDA, 2018). Regardless of whether it is a true margarine or a tablespread with less than 80% oil, the spread will be an emulsion composed of awater and an oil phase, and at least a portion of the oil phase will need to contain a solid fat to achieve the target spreadability and melting characteristics in the finished product (Chapman et al., 1960; Fomuso and Akoh, 2001; Sellami et al., 2012).

2.1.2. Baked Pastries

Baked pastries that use solid fats include pie crusts, cookies, biscuits, and laminated pastries like Danishes and puff pastries. The solid fat is able to interrupt the gluten matrix developed in dough that is made with cereal grain flours (Knightly, 1981; Baker and Mize, 1942; Baldwin et al., 1963; Harvey, 1937). The dough and its elasticity are caused by the gluten proteins making it a vital component in baked pastries (Hirahara and Simpson, 1961). However, overdevelopment of the gluten could give the finished baked product a texture that is too firm or chewy. Interference with the gluten matrix by solid fats creates a "shorter", less elastic dough that should produce a crumbly pastry with a soft, flaky texture (Finney et al., 1987; Souza et al., 1994; Lowe et al., 1938).

For laminated baked products like puff pastries, solid fat is required to create the distinct layers of dough that help to provide pastry lift and a flaky texture. The solid fat should be plastic during the dough mixing and folding time, which allows for the formation of distinct layers of dough and shortening. Water may be included in a puff pastry shortening blend at relatively low levels of 10% or 20% to release steam during baking for further lift (Kriz and Oszlanyi, 1976).

2.1.3. Icings and Fillings

Another application where solid fats play a key role is in icings and fillings in sweet baked foods. Solid fats provide structure to icings that are used to cover cakes, donuts, cookies, and other sweet pastries. Fillings generally have a similar composition as icings, but they are injected or layered within the confection. Plasticity is provided by the solid fat which allows the icing or filling to stay where it is applied. The ideal solid fat should allow the icing to be easy spreadable/injectable, provide a smooth texture, and quickly melt on the palette (Brody and Cochran, 1978).

Icings can be whipped to increase the volume, eating lightness, cost efficiency, and general aesthetic appeal. For whipped icings, it is important for the solid fat to provide enough solidity to hold its aerated structure without collapsing (Moncrieff, 1970).

2.1.4. Frying Shortenings

Another important application of solid fats is their usage in frying. Frying refers to cooking by immersing the raw food into a heated oil where the oil functions as a heat transfer medium. Unique traits of a food cooking via frying include an outer layer with a golden color and a crispy texture. These characteristics develop when the proteins and carbohydrates are heated, and dehydration occurs on this outer layer as heat drives off moisture in the form of steam. Besides its function as a heat transfer medium, the oil may also be absorbed into the food as a component that contributesto its flavor and mouthfeel (Choe and Min, 2007).

Oil oxidation occurs when oil reacts with oxygen and is accelerated in the elevated temperatures of frying (Peers and Swoboda, 1982; Cuesta et al., 1993; Houhoula et al., 2003). Saturated fatty acids in solid fats are less vulnerable than unsaturated fatty acids in liquid oils to oxidation during frying. By using these more stable oils, the fry life of the oil can be increased and in turn helps to improve efficiency with less time required to cycle the frying oils and less oil waste (Frega et al., 1999; Warner et al., 1994). The saturated fatty acids in solid fats are also less vulnerable than unsaturated fatty acids in liquid oils to polymer buildup during frying and therefore lead to improved fry life (Stevenson et al., 1984; Takeoka et al., 1997). Polymer buildup in the frying oil results in a number of undesired consequences including quicker oil degradation, poorer heat transfer, increased oil viscosity, and poor food color development (Choe and Min, 2007; Yoon et al., 1988; Yseng et al., 1996). Moreover, besides the increased stability of solid fats in frying applications, it may be desirable to use a frying oil with a melting point above that of the

temperature that the fried food will be served and consumed at. This would prevent an oily texture on the surface of the fried food.

2.1.5. Confectionary Fats

The characteristics of the solid fats used in chocolate and candies give confectionaries much of their desirable traits. Solid fats provide structure for the confectionary which allows for convenient packaging and handling at a consumer level (Ali and Dimick, 1994; Okawachi et al., 1985). When consumed, these fats should quickly melt at human body temperature to provide a desirable, non-waxy mouthfeel on the palate (Shukla, 1995).

2.2. Solid Fat Challenges

Despite of the importance of solid fats in many foods, a number of challenges can arise from their use. Preparation, handling, storage, melting, incorporation into foods, and nutrition are the areas in which solid fat difficulties could arise.

2.2.1. Preparation

A variety of methods are used to prepare solid fats for packaging, transportation, storage, and food incorporation. Totes or drums of solid fats require the use of elevated temperatures to melt the fats before being filled into the packaging, which would accelerate oil degradation (Crapiste et al., 1999). Cubes of the solid fats may be prepared by pouring the molten oil into cardboard corrugate box with an inner liner (Loughrin, 1987). Flakes may be created on chill rolls where a thin layer of fat is crystalized on a cooled cylinder before being scraped off (Ayers and Scott, 1950). Powdered and beaded fats can be prepared by grinding flaked fats or spray cooling. Spray cooling involves atomizing the fat into small particles in a sufficiently cold environment to rapidly crystalize the fat (McMichael, 1956). Time, specialized equipment, and temperature

adjustment energy are required for many of these processes which can lead to costly and inefficient preparation methods.

2.2.2. Handling

There are a number of factors that make solid fats more challenging to handle than liquid oils or other food ingredients. Solid fats are often packed in cubes or totes. Cubes can be heavy and difficult for operators to lift and add to batches. These cubes often use bag in box with an inner plastic liner that holds the fat inside a cardboard corrugate box (Loughrin, 1987). Because the solid fat is often poured into the packaging while liquid or molten, the liner must be carefully folded over it before the box is sealed. There is a possibility for the liner to sink into the molten fat before the fat crystallizes, which would lead to the liner mixing in the fat after full solidification. If entrapped in the fat, the liner can be difficult to disassociate from the solid fat causing inefficiencies to separate the two and potential foreign material contamination if the liner is not fully removed. Large cubes of solid fats can also cause splash out when dropped into liquid batches. Splash out can be hazardous for operators and may result in slipping or burns if the batch has been heated. Drums of solid fats will need to be stored at elevated temperatures or wrapped with an electric heating belt to melt the fats for removal. For large totes of solid fats, heavy equipment is typically required to transport the tote to ingredient batching areas and melting is often required to remove the fats from the tote (Zhou et al., 2011).

2.2.3. Storage

Elevated temperatures are needed for storage. At large-scale food production plants, solid fats may be stored in bulk tanks, but the tank must maintain a temperature at least above the melting point of the fat in order to pump it. The energy required for the high temperatures is costly, and over time, the high temperatures also accelerate oil degradation (Crapiste et al., 1999).

2.2.4. Melting

If solid fats are not stored at elevated temperatures, they may need to be remelted before transportation or incorporation into foods. Delays and inefficiencies are often caused by the remelting process before use. Costly energy and time are required to melt solid fats and the elevated temperatures accelerate oil degradation (Crapiste et al., 1999). A time-consuming waiting step is needed to allow the fat to melt so it can be uniformly dispersed throughout the ingredient mixture.

2.2.5. Uniform Incorporation into Foods

On an industrial scale, solid fats often must be packaged in large blocks or irregular shapes which make uniform incorporation into a food difficult. Liquid and free-flowing powder ingredients can easily be consistently blended into batches. In contrast, due to large or inconsistent sizes, solid fats present major challenges when blending uniformly and evenly into food batches. There is possibility for portions of the food to have little or no fat while have high concentrations of fat in other portions which would lead to poor and inconsistent finished product quality (Geisler, 1960).

Liquids and free-flowing powders can also be metered into foods in continuous production systems. Automated metering is difficult or impossible with blocks, totes, and flakes of solid fats which could limit their use to batch production processes (Byrn et al., 2014; Gao et al., 2011).
On a smaller foodservice or home kitchen level, solid fats handling can be challenging in a number of ways. Cold margarines or butter can be difficult to spread uniformly onto bread without the presence of butter clumps or potentially tearing the bread. When preparing baked foods like pastries, kneading the solid fat (butter and/or shortening) into the dough with proper uniformity

can be also challenging. If the solid fat is not properly dispersed into the dough, the baked food will have an inconsistent and poor texture.

2.2.6. High Calorie Contributions

Fat is a calorically dense macronutrient that provides 9 calories per gram of oil, which is over twice as much the 4 calories per gram in carbohydrates and protein (USDA, 2019). The sensory and functionality contributions of fat make it a critical ingredient necessary for many food formulas. For consumers looking to decrease their caloric intakes or food producers trying to reduce the calories in foods, the tradeoffs of using fat can be difficult to balance. The functionality and sensory traits of the fat are needed for a high-quality food, but the calories contributed by the fat can be undesirable (Drewnowski, 1992).

2.3. Attempts to Solve Solid Fat Challenges

The valuable functionality of solid fats combined with their usage challenges have led the food industry carry out various attempts to mitigate the challenges.

2.3.1. Heated Storage

One method to allow for easier solid fat handling, no melting wait time, and uniform incorporation into batches is to store and transport oil at elevated temperatures at least above its melting point. Consequently, the molten liquid oil can easily be pumped throughout a production facility and be mixed into liquid batches without the need for a long-waited melting step.

There are a few disadvantages of this approach. Costly bulk storage tanks are required to hold the oil at the production facility, and the energy required to maintain the elevated temperatures is also expensive. Regarding certain applications such as baked pastries, the fat may also need to be at solid state when incorporated into the dough for proper functionality and finished product

quality (Kriz and Oszlanyi, 1976). Finally, oil degradation will be accelerated at high temperatures, therefore long term storage of heated oils before use will not be viable (Crapiste et al., 1999).

2.3.2. Pumpable Shortenings

Pumpable shortenings are oil blends that contain some fat hardstock, but they are still liquid at room temperature, which allows to be pumped and incorporated into batches without additional heating. Typically, a pumpable shortening will be composed of a suspension of a solid fat in a liquid oil. Relative to solid fats stored at elevated temperatures, pumpable shortenings benefit from reduced storage energy costs, more flexible storage locations, and less oil degradation caused by high temperatures (Linteris and Thompson, 1958).

A limitation of pumpable shortenings is that only a portion of the blend is composed of the solid fat thus the full benefits of the standard solid fats to stability and functionality are not realized. Another limitation of pumpable shortening is the potential of an unstable suspension that could lead to oil stratification that may require storage with agitation to mitigate (Geisler, 1961).

2.3.3. Partial Hydrogenation of Oils

Partial hydrogenation of oils has been used to add stability and functionality to liquid oils. Partial hydrogenation provides more control over the melting and structuring characteristics of an oil than full hydrogenation which produces highly saturated fatty acids with limited functionality. This control over the fatty acid composition and characteristics of partially hydrogenated oils allows for customization, which makes them to be easier to handle, melt, and incorporate into foods than natively solid fats. The resulting monounsaturated fatty acids produced by partial hydrogenation provide improved stability over the liquid oil starting materials in applications like frying. The plasticity of the partially hydrogenated oils also allows for structuring and spreadability

in a number of foods including margarines, icings, fillings, baked foods, and confections (Balakos and Hernandez, 1997; Dietz and Scanlon, 2012).

However, the major problem with using partially hydrogenated oils in foods is the negative impacts of trans fatty acids on human health. The partial hydrogenation process produces monounsaturated trans fatty acids that have been shown in a large number of studies to significantly increase the risks of heart disease (Ascherio and Willett, 1997; Mozaffarian and Clarke, 2009; Vega-Lopez, 2006). These negative health effects have led the FDA to ban the use of partially hydrogenated fats in consumer foods (FDA, 2015).

2.3.4. Beads, Flakes, and Powders

Particles in the form of beads, flakes, and powders can be prepared from solid fats to improve ingredient handling and incorporation into formulas. Chill rolls can be used to produce flakes by metering a thin layer of fat onto a cooled cylinder where it is crystalized and scraped off (Ayers and Scott, 1950). Grinding flaked fats or spray cooling can be used to produce fat powders or flakes. The spray cooling process involves generating small fat particles via atomization of the molten lipid into a cool environment to rapidly crystallize the fat (McMichael, 1956).

However, production methods for fat particles can be costly and inefficient, and they will require specialized equipment, low temperature environment near the spray nozzle, and extendedtime for proper production (Ayers and Scott, 1950; McMichael, 1956). Another challenge is that the obtained particles are not uniform in terms of shape and size, with smaller particles falling at the bottom of the batch causing inconsistent and broad particle distribution. Moreover, nonuniform particles will not be free flowing, which would make pouring and batching with these particles difficult.

2.4. Potential Solutions Offered by Solid Lipid Particles Formed with Supercritical Carbon Dioxide

A relatively recent development in the creation of solid fat particles via supercritical fluid technology has brought interest for its potential benefits (Fahim et al., 2014; Lubary et al., 2011; Yang and Ciftci, 2016). A supercritical fluid is a fluid at pressures and temperatures above its critical point where it is not classified as a liquid or a gas but does possess the physical properties of both (Subramaniam, Rajewski, and Snavely, 1997; Nalawade, Picchioni, and Janssen, 2006; Montes, Gordillo, Pereyra, and Martinez de la Ossa, 2011). Supercritical fluids have viscosity, diffusivity, and compressibility characteristics that are similar to a gas, but also present density and solvent abilities similar to a liquid (Subramaniam et al., 1997; Nalawade et al., 2006; Montes et al., 2011; Brunner, 2005; Pasquali et al., 2008). Supercritical fluids' almost nonexistent surface tension, low viscosity combined with the high diffusivity allow for higher mass-transfer rates or penetration, therefore rendering supercritical fluids novel functionalities in lipid processing and applications. Carbon dioxide (CO_2) is the most common supercritical fluid because it has relatively low critical temperature and pressure (31°C, 74 bar), and it is nontoxic, nonflammable, environmentally friendly, inexpensive, and safe.

Previous studies have shown that solid lipid microparticles could be produced using particles from gas saturated solutions (PGSS) or gas assisted melting atomization (GAMA) (de Sousa et al., 2007; Mandžuka and Knez, 2008; García-González et al., 2010; Lubary et al., 2011; Bertucco, Caliceti, and Elvassore, 2007). A recent study has shown that hollow solid lipid micro- and nanoparticles could be produced from solid fats by atomization of the CO_2-expanded lipid via a nozzle (Yang and Ciftci, 2016).

In this process, upon depressurization, rapid cooling caused by the Joule-Thomson effect at the nozzle and the surrounding area allowed for crystallization of the CO_2-expanded liquid lipid bubble to generate hollow solid lipid particles (Yang and Ciftci, 2016). The obtained free-flowing hollow solid lipid particles could offer a number of novel benefits over traditional solid fat formats when preparing foods.

2.4.1. Production of Solid Lipid Microparticles Using Supercritical Carbon Dioxide

The lipids that were used to produce solid lipid microparticles in previous studies has been the ones that are solid at room temperature. Fully hydrogenated soybean oil (Yang and Ciftci, 2016) and fully hydrogenated canola oil (Ciftci and Temelli, 2016) have been reported to form solid lipid microparticles based on the PGSS process. When mixed with pressurized CO_2, the melting point of the solid fat will decrease due to the CO_2 dissolution, which allows for a reduced temperature processing in the high-pressure expansion vessel to achieve low energy consumption and lower processing cost (Ciftci and Temilli, 2014). Recently, Ciftci and Temelli (2014) reported the melting point depression of solid lipids in pressurized CO_2. In that study, melting point depression of pure solid lipids of different classes (stearic acid, monostearin, tristearin, lauric acid, and trilaurin) and fats (fully hydrogenated canola oil and coconut oil) were investigated in pressurized CO_2 up to 350 bar. A linear decrease in melting point was observed with increasing pressure at relatively low to moderate pressure regions. Moreover, Yang and Ciftci (2016) reported a similar melting point depression of fully hydrogenated soybean oil in pressurized CO_2. The melting temperature of fully hydrogenated soybean oil decreased from 68.5 º C at atmospheric condition to 57.2 º C at 122 bar. Generation of melting curves provides valuable information that allows us to know the lowest temperature and pressure at which the solid lipid would melt.

Custom designed equipment has been used for the particle formation system. A previous reported system was composed of a high-pressure syringe pump, a pre-heating section, a high-pressure expansion vessel, temperature controllers, pressure gauge, a magnetic drive, a depressurization valve, and a spray nozzle (Yang and Ciftci, 2016). The selected lipid or lipid blend will be fully melted on a hotplate before injected into the high-pressure expansion vessel through the sampling port. The syringe pump is used to pressurize the expansion vessel with CO_2, and the expansion vessel temperature is set to the lowest melting temperature of the lipid at the selected pressure to ensure the lipid is in a liquid state in the vessel. The temperature of the depressurization valve and nozzle will be set at a relatively high temperature to avoid lipid crystallization via the Joule-Thomson effect when exiting the spray nozzle. After 1 hour of mixing at 1000 rpm by the magnetic drive, a CO_2-expanded lipid is formed in the vessel due to CO_2 dissolution in the lipid. Then the magnetic drive is turned off to allow to stabilize for 10 min. Afterwards, the pressure is set at 10 bars above the processing pressure and the depressurization valve is quickly opened to atomize the CO_2-expanded lipid through the nozzle. Free-flowing solid lipid microparticles will then be collected until analysis (Yang and Ciftci, 2016).

2.4.2. Characteristics of Solid Lipid Microparticles

The obtained solid lipid microparticles have a number of characteristics that are unique relative to the raw lipid starting materials. The solid lipid microparticles have been shown to be hollow, spherical, and free-flowing with high loading capacity and no expelling (Yang and Ciftci, 2016). Pressure and nozzle diameters significantly affected the particles' attributes including particle morphology, particle size and size distribution, melting properties, and polymorphism (Yang and Ciftci, 2016). Yang and Ciftci (2016) concluded that the optimal processing condition to obtain the smallest hollow spherical particles ($d_{50\%}$ = 278 nm) was 200 bar and 50 μm nozzle

diameter. In addition, the melting temperature of the solid lipid microparticles also decreased relative to the bulk lipid and was attributed to the small particle size with high surface area, the hollow structure with the thin shell, and polymorphic form transition from β and β' to α (Yang and Ciftci, 2016). The hollow cavity of the solid lipid microparticles and the spherical uniformity could become more pronounced with an increasing melting point of the lipid material. Moreover, the bulk density of the solid lipid microparticles is expected to decrease significantly compared to the original raw lipid material, which could be caused by the hollow structure, the small size, and the packing spaces between the particles. All of these unique attributes of the hollow solid lipid microparticles would be able to offer a number of benefits over traditional solid fat formats when preparing foods.

2.4.3. Simple Uniform Incorporation into Foods

Traditional solid fat formats often require some preparations such as melting or cutting to small pieces before added to a food, but the small size and free flowing properties of the hollow solid lipid particles could simplify the process. In the case of baked products, it would be relatively simple to blend the hollow solid lipid particles into the flour that is used for the dough rather than melting or cutting a standard solid fat for incorporation (Geisler, 1961). Fat distribution is important when trying to mimic meat characteristics in vegetarian meat analogues (Kempster, 1981; Tingle et al., 1995). Small solid fat particles could achieve uniform distribution in a meat analogue. At a consumer level, potential benefits of using hollow solid lipid particles include a tablespread-like product that could be packaged in a shaker for easy addition to foods or recipes without the need to cut a butter stick or scoop out of a margarine tub.

2.4.4. Rapid Remelting

The small, hollow solid lipid particles possess a high ratio of surface area to mass relative to larger, bulk solids. Studies have shown that particle size has a major impact on the melting temperature of colloidal substances; the melting temperature decreased with decreasing particle size (Defay et al., 1966, Yang and Ciftci, 2016). In a powdered drink mix or powdered creamer, the high ratio of surface area to mass could allow for more direct contact with the warm liquid and facilitate quicker melting and mix in. This trait could also provide benefits during consumption. The fat would melt quicker on the palate to help provide a more desirable liquid fat mouthfeel rather than the waxy mouthfeel that may come from high melting fats which maintain at the solid state after consumption.

2.4.5. Easy Handling

Free-flowing particles are easily be moved, poured, and weighed in ways that are familiar to industrial food plants that typically handle other powders like salt and sugar. Packaging options could be flexible and potentially viable with boxes, pails, buckets, totes, and super sacks. The small particle size would help to minimize the risk of possible splash out when added to liquid batches. With individual particle masses that are a fraction of a gram, precise addition and nearly exact formula weights could be achieved when batching ingredients.

2.4.6. Use in Continuous Production Systems

Bulk solid fats and fat particulates that are non-uniform or not free flowing typically require a batch processing at industrial food production scales due to difficulties in accurately metering solid fats into foods. However, free-flowing solid lipid particles can unlock the potential of using vibratory or screw feeders for efficient incorporation into formulas during continuous production (Byrn et al., 2014; Gao et al., 2011).

2.4.7. Lower Fat Material Usage and Reduced Calories

The small size and hollow nature of the solid lipid particles could also provide benefits in reducing oil usage in formulas (Yang and Ciftci, 2016). The relatively high ratio of surface area to mass allows to use smaller amounts of oil particles while engaging a more direct contact with other ingredients in a food matrix. In foods such as shortened pastries or fat structured confectionaries where the fat functionality requires contact with other ingredients, reduced fat levels may be achievable while still maintaining the desired functionality (Knightly, 1981; Baker and Mize, 1942; Baldwin et al., 1963; Harvey, 1937). Moreover, the hollow feature and small size would decrease the density of the spherical solid lipid particles, and therefore, less lipid particles are needed than bulk fats to meet the same volume of a food in a package. From sensory perspective, fat plays a vital role in the desirable mouthfeel and flavor of a food (Drewnowski, 1992). Potentially less fat material may be needed to provide the same desirable traits if the fat has relatively more surface area to coat the palate. Major benefits of reduced oil usage include fewer nutritional calories and lower formula costs for both food manufacturers and consumers.

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CHAPTER 3. FORMATION OF LOW DENSITY AND FREE-FLOWING HOLLOW MICROPARTICLES FROM BUTTER AND FRACTIONATED PALM OIL*

3.1. Abstract

The use of solid fats is challenging due to difficulty in incorporating into foods, handling during industrial food production, and relatively high calorie contributions. The objective of this study was to form free-flowing and low density hollow microparticles from nonhydrogenated fats, namely, butter and fractionated palm oil, using a novel method based on atomization of a carbon dioxide (CO_2)-expanded lipid mixture. Melting point of the fractionated palm oil decreased from 66.2 to 47.3 °C above 120 bar in the presence of pressurized CO_2. The density of the particles decreased 5 folds compared to that of the original oils. Particle size decreased with increasing fractionated palm oil content. Ten percent ($d_{10\%}$) and fifty percent ($d_{50\%}$) of the 100% palm oil particles were smaller than 4.49 μm and 23.0 μm, respectively, whereas they were 14.5 μm and 58.3 μm when mixed with butter at 50% butter concentration, respectively. The hollow structure was more pronounced for the particles obtained from higher melting oils/oil blends, as well as with more spherical uniformity. Polymorphic form of α was more pronounced in the solid lipid particles, indicating that they had a less ordered crystalline structure than the original oil. This new method forms low density and free-flowing lipid powders that make the handling and storage of solid lipids feasible and convenient. Nonhydrogenated lipid particles could have unique applications in the food industry including easier handling of solid fats, uniform fat incorporation into foods, reduced fat usage, reduced calorie intake, and more rapid oil melting in mouth.

Keywords: Fractionated palm oil; Butter; Hollow solid lipid particle; Supercritical carbon dioxide; Melting.

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3.2. Introduction

Although solid fats are critical components of many foods, their use can present a number of challenges. In industrial food production, solid fats like butter and shortening can cause process inefficiencies. They are often packaged and stored in cubes or large totes that can be difficult to handle. Totes of solid fats require the use of heavy equipment to transport to ingredient batching areas and usually need to be melted before incorporation into the batch. Cubes of solid fat are heavy and difficult for operators to add during batching. After being added to a batch mixture, many production procedures will then require a time-consuming waiting step to allow the solid oil to melt so it can be evenly dispersed throughout the ingredient mixture. Solid fats may also be stored in large bulk tanks at production plants, but bulk tank storage requires the oil to be heated above its melting point to be pumped. These elevated temperatures require costly energy to maintain and can also accelerate oil degradation. At a consumer level, cold butter can be difficult to spread evenly onto bread without the presence of butter clumps or potentially tearing the bread. When preparing baked goods like pastries, kneading butter and/or shortening into the dough can also be problematic. If the solid fat is not properly dispersed into the dough, the baked good will have an inconsistent and undesirable texture. A potential solution to these challenges is to create small solid fat particles that are free-flowing, easy to handle, and simple to be incorporated into foods.

Exciting role of supercritical fluid technology for particle formation attracted interest in the recent years (Fahim et al., 2014; Lubary et al., 2011; Yang and Ciftci, 2016). Carbon dioxide

(CO_2) is the most common supercritical fluid because it has mild critical temperature and pressure (31 ºC, 74 bar), and it is nontoxic, non-flammable, environmental friendly, inexpensive and safe. Previously, micron size solid lipid particles were generated using particle from gas saturated solutions (PGSS) or gas assisted melting atomization (GAMA) methods (Sampaio de Sousa et al., 2007; Mandžuka and Knez, 2008; García-González et al., 2010; Lubary et al., 2011; Bertucco et al., 2007). Lubary et al. (2011) used a similar process called supercritical melt micronization to form and collect the particles from non-chemically modified low melting lipids, namely, anhydrous milk fat and a diacylglycerol-based modified milk fat. A potential challenge of that method was the development and maintenance of a low temperature environment in the sample collection vessel which could be resource-intensive on an industrial scale. In addition, using low melting lipids requires material handling at refrigerated temperatures after particle formation. Recently, Yang and Ciftci (2016) reported formation of hollow solid lipid micro- and nanoparticles from fully hydrogenated soybean oil via atomization of a CO_2-expanded solid lipid through a nozzle. In the process of Yang and Ciftci (2016), upon depressurization, the Joule-Thomson effect caused cooling at the nozzle and the surrounding area which allowed for crystallization of the liquid lipid bubble to form hollow solid lipid particles (Yang and Ciftci, 2016). To successfully produce solid lipid particles, the lipid material must have a melting point sufficiently above the ambient temperature where the CO_2-expanded lipid is being depressurized and atomized. Even though fully hydrogenated oils are suitable candidates for lipid particle formation using the method recently reported by Yang and Ciftci (2016) due their composition of mostly a single triacylglycerol (around >85% stearic acid for fully hydrogenated soybean oil) and therefore sharper melting point, a potential issue with using hydrogenated oils is that many consumers have an aversion to seeing hydrogenated oils on a food's ingredient statement (Cargill, 2017).

Nonhydrogenated oils and their blends are potential candidates to form such lipid particles but their behavior during particle formation via atomization of CO_2-expanded lipid is not known due to the wide melting range of nonhydrogenated oils resulting from presence of a number of different triacylglycerols.

Therefore, the main objective of this study was to investigate the formation of free-flowing and low density lipid microparticles composed of non-hydrogenated oils that can provide benefits such as easy handling, simple incorporation into foods, and improved food quality. Specific objectives were to: (i) form dry hollow solid lipid microparticles from fractionated palm oil and low moisture butter using CO_2; (ii) determine the melting behavior of fractionated palm oil and low moisture butter in pressurized CO_2; and (iii) characterize the particles in terms of particle morphology, particle size and size distribution, particle density, melting properties, and polymorphism.

3.3. Materials and Methods

3.3.1. Materials

Fractionated palm oil was acquired from Loders Croklaan B.V. (Channahon, IL, USA). Low moisture butter was acquired from Dairy Farmers of America Inc. (Kansas City, KS, USA). CO_2 (99.99% purity) was purchased from Matheson (Lincoln, NE, USA).

3.3.2. Preparation of the fractionated palm oil and butter blends

Fractionated palm oil and low moisture butter were separately melted on a hotplate at 130 ºC for 20 minutes to erase crystal memory. Then, oil blends were prepared by uniformly mixing fractionated palm oil and butter to obtain 25%, 50%, and 75% (v/v) butter contents in the blends.

3.3.3. Determination of melting behavior of the solid lipids in pressurized carbon dioxide

Melting behavior of the fractionated palm oil and butter in pressurized CO_2 was studied in a jacketed high-pressure vessel according to Yang and Ciftci (2016). The high-pressure vessel was equipped with two sapphire windows, a microscope, a camera, and a refrigerated circulator (model 1162A, VWR Inc., Radnor, PA, USA). Circulating bath was used to control the temperature of the vessel by circulating hot and cold water through the jacket of the vessel. Each lipid sample was completely melted as described in section 3.3.2., and 100 µL of the molten lipid was placed into a 200 µL glass gas chromatograph (GC) vial insert. Then, the GC vial insert was placed in a glass transparent vial and then positioned in the vessel chamber between the two sapphire windows. CO_2 was used to pressurize the vessel via a syringe pump (Model 250D, Teledyne Isco Inc., Lincoln, NE, USA). The molten lipid sample was stabilized in the pressurized chamber for 1 h. Then, the temperature of the vessel was decreased to 5 ºC below the solidification temperature of the lipid, which was observed using the microscope-camera system. After 5 min of complete solidification, temperature of the vessel was increased at a rate of 0.3 ºC/minute to observe the first melting point of each lipid sample. The first melting temperature and corresponding pressure were recorded.

3.3.4. Production of hollow solid butter-palm oil microparticles using carbon dioxide

A custom-made particle formation system was used to produce free flowing hollow solid lipid microparticles from fractionated palm oil and its blends with low moisture butter. Details and operation of the particle formation system was reported previously (Yang and Ciftci, 2016). Briefly, the system contained a high-pressure syringe pump, pre-heating section, 100 mL high-pressure expansion vessel, magnetic drive, temperature controllers, depressurization valve, and a nozzle. Temperature of the expansion vessel was set to the lowest melting point of the solid lipid in pressurized CO_2 at 200 bar where the solid lipid is in its liquid state. Our previous studies

showed that 200 bar and 50 μm nozzle diameter generated smaller ($d_{50\%}$= 278 nm) hollow spherical particles (Yang and Ciftci, 2016); therefore, 50 μm-diameter nozzle was used. Temperature of the depressurization valve and nozzle was set to 130 ºC to prevent freezing due to Joule-Thomson effect during atomization.

Firstly, fractionated palm oil or its blends with butter was fully melted at 130 ºC, and then 20 mL of the molten lipid sample was manually injected into the expansion vessel via the sampling port. Then, the expansion vessel was pressurized to 200 bar with CO_2 using the syringe pump. The pressurized CO_2 and lipid sample were mixed at 1000 rpm for 1 h using the magnetic drive to form a CO_2-expanded lipid. The mixture was then allowed to stabilize for 10 minutes after the magnetic drive was stopped. The pressure of the syringe pump was set to 10 bar above the pressure of the expansion vessel, the inlet valve was opened, and the depressurization valve was opened immediately, which allowed the CO_2-expanded lipid to be atomized through the nozzle. Finally, solid lipid particles were formed and collected in the sample collection vessel.

3.3.5. Fatty acid analysis

The fatty acid composition of the fractionated palm oil, low moisture butter, palm oil-butter blends, as well as the obtained solid lipid particles was determined according to AOAC Method 996.06 (AOAC, 1997). Each sample (200 mg) was heated above its melting point, and 2 mL of triundecanoin ($C_{11:0}$) solution (5 mg/mL in chloroform) was added as an internal standard. Samples were dissolved in a 1:1 blend of chloroform and diethyl ether. A 14% BF_3/methanol reagent was added with toluene and the mixture was heated at 100 °C in an oven for 45 minutes. After the mixture has been allowed to cool to room temperature, water (5 mL), hexane (1 mL), and sodium sulfate (1 g) were added. Layers of the mixture were allowed to separate, and the top layer containing fatty acid methyl esters was transferred for analysis. Fatty acid methyl esters were

analyzed using a capillary gas chromatograph equipped with a hydrogen flame ionization detector. Separation was performed on a capillary column composed of fused silica (SP-2560; 100 m x 0.25 mm with 0.20 µm film thickness). Helium with a flow rate of 0.75 mL/minute was used as the carrier gas. The injector and detector temperatures were set at 225 °C and 285 °C, respectively. The initial column temperature was 100 °C and held for 4 minutes before ramping at 3 °C/minute to a final temperature of 240 °C which was held for 15 minutes. Identification was done by comparing the retention times of the peaks with those of authentic fatty acid standards.

3.3.6. Particle size and size distribution

A particle size analyzer based on laser diffraction (Mastersizer 3000, Malvern Instruments Ltd., Worcestershire, UK) was used to measure the particle size and size distribution of the solid lipid particles. Approximately 30 mg of solid lipid particles were suspended in 25 mL distilled water with the addition of 0.4% (w/w) of polyoxyethylene sorbitan monooleate (Tween 80). Suspensions were then sonicated 30 min in an ultrasonic water bath (3510 R-MTH, Branson Ultrasonics Corporation, Danbury, CT, USA) before analysis. The range of 5% - 7% was used as the obscuration value. The refractive index (RI) of the lipid sample was set as 1.46. Distilled water (RI = 1.33) was used as the dispersant.

3.3.7. Particle morphology

3.3.7.1. Scanning Electron Microscope (SEM) analysis

Particle morphology of the solid lipid particles was analyzed by a Field Emission-Scanning Electron Microscope (FE-SEM) (S4700, Hitachi High-Technologies Corporation, Japan). Double-sided carbon tape was used to mount a thin layer of the solid lipid particles. Then, a HiPace 80 (Pfeiffer Vacuum, Germany) sputter-coated the lipid samples with chromium in argon atmosphere.

Particles were also freeze fractured prior to SEM imaging to present the hollow structure. The imaging was carried out at room temperature (21 °C).

3.3.7.2. Atomic Force Microscopy (AFM) analysis

The AFM analysis was performed ot quantify the surface roughness of the palm oil-butter particles. The same samples used for SEM imaging were used for AFM analyses. AFM experiments were conducted using a Bruker Dimension Icon AFM with ScanAsyst automatic image optimization mode based on PeakForce Tapping (Santa Barbara, CA, USA). ScanAsyst-Air probe (k ~0.4 N m−1, tip radius < 10 nm) (Bruker Corporation, Santa Barbara, CA, USA) was employed in all AFM measurements. The oscillation frequency was 2 kHz. All images were recorded in air and under atmospheric conditions (22 °C, 25% RH). The scanning field was kept at 10 μm by 10 μm for all the particle samples. Two dimension (2D), three dimension (3D), and roughness data were acquired from the Nanoscope software package (Bruker Corporation, Santa Barbara, CA, USA). The morphology of the surface sample was characterized by the arithmetic mean surface roughness (R_a):

$$R_a = \frac{1}{n}\sum_i^n \left| Z_i - Z_{\text{ep}} \right|$$

Z_{ep} is the height of the center plane, and Z_i is the *i*th height sample out of n total samples, as Z_i tends toward Z_{ep} surface roughness decreases. *n* is the number of samples within a given area.

3.3.7.3. Confocal fluorescence microscopy analysis

The distribution of butter in hollow solid lipid particles of fractionated palm oil was investigated by using a confocal fluorescence microscope (A1, Nikon Instruments Inc., Japan). Approximately 3-5 mg of solid lipid particles were firstly stained using 40 μL Nile Red solution

(0.125%, w/v, in propane-1,2-diol) for 40 min before image collection. A fluorescence microscope (90i, Nikon Instruments Inc., Japan) was then used to record confocal images of z-series scanning by distance increments of 1.0 μm. Number of images was 14, 15, and 26 for particles obtained with only fractionated palm oil, 75% fractionated palm oil, and 50% fractionated palm oil, respectively. Excitation wavelengths of 561.6 and 640.9 nm and emission wavelengths of 570–620 and 663–738 nm were set to conduct the analysis for red and blue fluorophores, respectively. The imaging was carried out at room temperature (21 °C).

3.3.8. Determination of the particle density

The bulk density (β) was determined in a 25 mL glass graduated cylinder as described by Quispe-Condori et al. (2011). Approximately 3 grams of each sample (m) was weighed and poured through a funnel into the cylinder. The cylinder was then slightly tapped to collect the powders sticking to the cylinder wall off. The volume (V) was read directly and used to calculate the bulk density ($\beta = m/V$).

3.3.9. Determination of melting properties

Melting profile of the fractionated palm oil, low moisture butter, blends, and the solid lipid particles were determined using a differential scanning calorimeter (Pyris 1, Perkin Elmer, Waltham, Massachusetts, USA). A hermetically sealed stainless-steel pan was used to hold 5-7 mg of the samples, while an identical empty sealed pan served as the reference. The sample and reference pans were set in the calorimeter and allowed to equilibrate for 1 minute at 25 ºC. Then, the samples were heated from 25 ºC to 100 ºC at a heating rate of 5 ºC/minute.

3.3.10. Determination of polymorphism

Polymorphism of the solid lipid particles was determined using a PANalytical Empyrean Diffractometer unit (Empyrean, PANalytical, Westborough, MA, USA). The unit was operated with Cu Kα radiation with an intensity of 45 mA and a voltage of 40 kV. The incident beam path had a 20 mm mask and a divergence slit of 1/8 degree. The solid lipid particles were placed in a stainless-steel holder with a 27 mm diameter and a pocket that is 2 mm deep. To improve the signal to noise ratio, the PIXcel detector had a diffracted beam monochromator. A spin rate of 22.5º/s was used during analysis. The continuous scan was run from 2 to 50º at 2θ/minute with a step size of 0.026.

3.3.11. Statistical analysis

Data are presented as mean ± standard deviation based on triplicate experiments and analyses. A single factor ANOVA was used to analyze differences within each Differential Scanning Calorimetry (DSC) data (onset melting temperature, peak melting temperature, offset melting temperature, and enthalpy value) among the samples (fractionated palm oil, low-moisture butter, their physical blends, and the obtained particles). SAS version 9.3 was the statistical software package used for all analyses (SAS Institute Inc., NC, USA). An alpha level of <0.05 was used to denote significance. Post hoc test was conducted by using Tukey's multiple comparison.

3.4. Results and Discussion

3.4.1. Melting behavior in pressurized CO_2

Understanding the melting behavior of the solid lipids in pressurized CO_2 is the key to select the lowest processing temperature to form particles via atomization of CO_2-expanded lipid. Previously, it was shown that the melting point of the fully hydrogenated canola oil decreased from 71 to 58 °C in the pressurized CO_2 above 122 bar (Ciftci and Temelli, 2014), and that of

fully hydrogenated soybean decreased from 68.5 to 57 °C above 120 bar (Yang and Ciftci, 2016). Melting behavior of the fractionated palm oil and low moisture butter in pressurized CO_2 is shown in Figure 3.1. Melting point of the fractionated palm oil was 62.2 ºC at atmospheric conditions; however, it decreased to 47.3 ºC above 120 bar in pressurized CO_2. Similarly, melting point of the low moisture butter was 33.5 ºC at atmospheric conditions, and it decreased to 22.8 ºC above 55 bar. During mixing of the pressurized CO_2 and lipid, CO_2 dissolves in the liquid lipid and forms a CO_2-expanded lipid due to the dissolution of CO_2 in the lipid (Yang and Ciftci, 2016). Therefore, in the high-pressure expansion vessel, two phases were formed; the upper SC-CO_2 phase consisting of mainly SC-CO_2, and the bottom CO_2-expanded lipid phase. Only the bottom CO_2-expanded lipid phase is responsible for particle formation. The volumetric expansion of the lipids was reported previously to confirm the development of CO_2-expanded lipids (Ciftci and Temelli, 2014). Results confirmed that the lipid samples were in the liquid state during the expansion stage of the particle formation process. A CO_2-expanded lipid mixture is obtained due to dissolution of pressurized CO_2 in the lipid phase; therefore, the lipid must be in the liquid state to dissolve CO_2 in the lipid phase and to form an expanded lipid mixture. Melting point depression in pressurized CO_2 is important to optimize the particle formation conditions, and low processing temperature will also decrease the energy usage in the food industry.

3.4.2. Particle morphology of the hollow solid lipid microparticles

SEM images of the solid lipid microparticles obtained with fractionated palm oil and its blends with low moisture butter are shown in Fig. 3.2. All generated particles were spherical and free-flowing. The hollow structure of the particles generated at all palm oil levels was observed from the SEM images of the freeze-fractured particles (Fig. 3.3.). The particles had a wrinkled surface and increasing the butter content increased the wrinkled surface. Wrinkled surface

formation was mainly due to melting point differences between butter and the fractionated palm oil. Butter has a lower melting temperature (38 ºC) than fractionated palm oil (67.7 ºC). When the CO_2-expanded lipid mixture is atomized at the nozzle upon depressurization, a liquid droplet of fractionated palm oil, butter and SC-CO_2 was formed and then turned into a liquid lipid bubble due to CO_2 expansion at atmospheric pressure. In the meantime, temperature of the atomized particles decreased quickly due to Joule-Thomson effect (Yang and Ciftci, 2016, 2017). Fig. 3.4. presents the 3D surface topography of the palm oil-butter microparticles. The scale for 100% fractionated palm oil particles was 0–230 nm, whereas it was set at 0–1000 nm for 75% and 50% fractionated palm oil particles to include more specific details, and therefore rendering images a higher resolution. In agreement with the SEM images, the roughness and wrinkles on the particles' surface increased with increasing butter content in the lipid mixture. The mean surface roughness of the particles obtained with 100%, 75%, and 50% palm oil in the mixture was 21.9, 51.2, and 104 nm, respectively. When the higher melting fraction (palm oil) solidified, the lower melting fraction (butter) was still liquid and CO_2 was leaving the bubble toward outside, disturbing the smooth surface. Immediately after CO_2 released, the particle solidified and formed a wrinkled surface. The higher the solubility of CO_2 in the lipid phase, the higher wrinkled surface formation is expected because dissolution of the CO_2 in the lipid determines the melting point depression, which, in turn, determines the degree of the solidification rate. A faster solidification rate will form less wrinkled surfaces compared to slow solidification. It was reported that the SC-CO_2 had higher solubility in the lower melting fats than that of the higher counterparts, resulting in higher volumetric expansion (Ciftci and Temelli, 2014; Jenab and Temelli, 2012). Previously, it was found that the volumetric expansion of fully hydrogenated canola oil at 63 °C and 150 bar was 12%, whereas it was 36% for cocoa butter (Calvignac et al., 2010; Ciftci and Temelli, 2014). When

the butter concentration in the lipid mixture was increased, more CO_2 dissolved and the lipid droplet during atomization contained more CO_2. Therefore, more force was exerted on the inside of the liquid lipid bubble. During atomization, the quicker, more compact particle formation without butter did not allow wrinkles to form as prominently as it did in the slower solidifying butter-containing blends. With certain portions of the blend solidifying at different rates, the protruding portions of the sphere can be created. In addition to SEM images, confocal fluorescence microscopy z-series scanning images that show the cross section of the spherical particles revealed that the microparticles were hollow (Fig. 3.5.). Fig. 3.5. illustrated images taken at only a single slice during the z-series scanning of the particles, with a slice at the exact central location of the scanning in Fig. 3.5. (a, b, c) and a slice with a deeper scanning downward in Fig. 3.5. (d, e, f). The images in Fig. 3.5. (d, e, f) were auto-adjusted to improve the contrast to show the hollow structure of the particles. Some particles had one single large pore (hollow), and some particles had multiple relatively smaller pores (Fig. 3.5. a, b, c) and when subjected to z-series scanning, these pores merged and created a big hollow sphere inside of the particle shell (Fig. 3.5. d, e, f). Nile Red fluoresces differently depending on the degree of hydrophobicity of lipids, i.e., polar lipids such as phospholipids vs. neutral lipids such as triacylglycerols (Daemen et al., 2015; Diaz et al., 2008). The Nile Red psuedocolored blue/red ratio could be used to differentiate lipids (Diaz et al., 2008). The addition of butter to fractionated palm oil appeared as a brighter red color, because the fluorescent dye picked up both oils for staining. In addition, such a brighter color could also be due to slightly different emission intensities when bound to butter compared to fractionated palm oil. As expected, a higher butter content (50%) in the starting oil blend resulted in an increase in the red color intensity in the shell of the solid lipid particles, whereas there was no clear observation of the increased red color intensity in the hollow cavity.

3.4.3. Particle density

Bulk density is a quality control parameter to assess the powdered particles. A dry product with high bulk density can be stored in small containers at the same amount to a product with low bulk density. The bulk density of the solid lipid particles obtained at different lipid levels is listed in Table 3.1. The bulk densities found in this study were typical of encapsulated powders (Onwulataet al., 1996) with a few exceptions including microcapsules of a mixture of oil and acacia gum (Fuchs et al., 2006) and butteroil and modified corn starch (Onwulata et al., 1996). It was observed that the particles from the fractionated palm oil and the lipid matrix drastically reduced its bulk density (141-169 kg/m^3) compared to their physical mixture counterparts (865-880 kg/m^3). The average bulk density of fractionated palm oil particles, 25% butter particles, and 50% butter particles was reduced by 80.5%, 83.5%, and 83.9%, respectively, when the solid physical blends were transformed into hollow solid lipid particles. The density reduction was caused by the hollow structure, small size of the particles as well as the packing spaces among the particles. Moreover, solid lipid particles produced from fractionated palm oil were denser (169 kg/m^3) than the particles with butter blends (141 kg/m^3 for 50% butter). When used in food products, this reduction in density could provide key benefits. Less lipid material can occupy more volume which could allow for reduced material usage in food products with a fixed volume. The reduced material usage can also positively impact the nutrition of the food by reducing the number of fat grams and overall calories. The application of the particles obtained in this study could especially be impactful in lipids which have a high caloric density relative to other macronutrients.

3.4.4. Particle size and size distribution

All particles exhibited a similar bimodal size distribution, which consisted of both nanoparticles and microparticles (Fig. 3.5.). The mean particle size increased with butter content

in the non-hydrogenated oil blends. The smallest particles were produced from the 100% fractionated palm oil (D [4, 3] = 27.1 μm). Ten percent ($d_{10\%}$) and fifty percent ($d_{50\%}$) of the particles were smaller than 4.49 μm and 23.0 μm, respectively, whereas they were 14.5 μm and 58.3 μm at 50% butter concentration, respectively (D [4, 3] = 67.0 μm). A likely cause of the increasing particle size with higher levels of butter was the impact of the butter on the melting properties of the solid lipid particles, which in turn affected the solidification rate during particle formation (Yang and Ciftci, 2016). The addition of butter reduced the melting point of the particles, which solidified slower during particle formation. The solidification rate was lower at increased butter concentrations due to lower melting point of the butter compared to the fractionated palm oil; the lipid bubble had more time to expand during atomization due to CO_2 release from the lipid bubble and formed larger hollow particles. It should be noted that the particle size results may be affected by the particle agglomeration in the samples with more butter content as well; therefore, it must be compared with the particle morphology analyses. When SEM images were compared, it was observed that the particle agglomeration occurred for all blends (Fig. 3.2.). In addition, when confocal images were compared, the extent of particle agglomeration increased with butter concentration (Fig. 3.5.). This was due to the blends of fractionated palm oil and butter made the lipid mixture viscous and the obtained particles sticky upon particle formation. However, particles generated at 50% butter content were still free-flowing at room temperature. Previously, Yang and Ciftci (2016) reported average particle sizes (D [4,3]) of 3.9-13.1 μm for the particles obtained from fully hydrogenated soybean oil with the same process. Rodrigues et al. (2004) formed theophylline/hydrogenated palm oil particles with mean particle diameter of 3 μm using the PGSS technique; however, they did not report a hollow structure and the particle size were only micron range.

3.4.5. Melting properties

The melting properties of the fractionated palm oil and its blends with low moisture butter are important to understand the characteristics of the obtained solid lipid particles including size distribution, particle morphology, and polymorphism. Table 3.2. presents the DSC melting points of the original nonhydrogenated oils and their blends, the generated solid lipid particles from fractionated palm oil and its selected mixtures with low-moisture butter, respectively, and Fig. 3.7. shows the DSC melting curves of the solid lipid particles. The major melting point of the fractionated palm oil was higher than that of the blends with low-moisture butter that possessed the lowest. Moreover, with increasing levels of butter to fractionated palm oil from 25% to 75%, the melting peak temperature of the physical blends significantly decreased from 65 to 58 °C ($P < 0.05$) due to the presence of more unsaturated fatty acids making the mixture in a less-ordered packing with less solid fat content (Table 3.3.). After the particle formation process, even though the fatty acid compositions were similar, solid lipid particles exhibited a different melting profile compared to their physical bulk oil. The original fractionated palm oil and its blends with butter, which was at 25% and 50% concentration, had a major melting peak temperature around 60–67.7 °C, whereas the solid lipid particles exhibited a stepwise melting pattern and shifted the melting temperature to a relatively lower temperature. The original fractionated palm oil melted between 62 and 69C with a major endothermic peak of 67.7 °C; however, the single endothermic melting peakwas significantly reduced to 61 °C for its solid lipid particles counterpart ($P < 0.05$). A similar significant decrease in the major melting peak temperature was also observed for lipid particles obtained from 25% and 50% butter concentrations ($P < 0.05$). This major melting peak temperature decrease was attributed to the smaller particle size, hollow structure with a thin shell, and polymorphic forms (discussed below in Polymorphism Section). In solid lipid particles from

nonhydrogenated oil blends, two melting peaks were depicted, with 53 °C being the lower peak for both oils and 55.5 or 60°C being the second peak, depending on the lipid composition. The presence of the lowest melting peak of 53 °C was attributed to the nanosize portion of the lipid particles (Yang and Ciftci, 2016). Particle size plays a crucial role in melting temperature of colloidal substances; melting temperature decreases with decreasing particle size (Defay et al., 1966). Interestingly, no melting peak of 53C shown in lipid particles of fractionated palm oil. This was due to the agglomeration of the nanoparticles. The presence of nanoparticles in the solid lipid particles was evidenced in the particle size analysis (Fig. 3.6.). Moreover, the addition of a less saturated fat, i.e., low-moisture butter, to fractionated palm oil resulted in formation of a relatively less-ordered crystals of the lipid particles and led to a significant reduction in the melting point ($P < 0.05$). This phenomenon became more pronounced when 50% butter mixed with the fractionated palm oil, the major melting peak temperature decreased to 55.5 °C compared to 61 and 60 °C at 0% and 25% butter concentrations, respectively.

3.4.6. Polymorphism

Polymorphism is an important parameter that affects the melting properties of the solid lipid particles. Fats can crystallize in three main polymorphic forms, namely α, β, and β'. The polymorphic form of α is the least stable whereas β is the most stable, and β' is metastable (Rousseau, Marangoni, & Jeffrey, 1998). Polymorphic form of α melts at a lower temperature than β' and β forms, which is due to less-organized packing of triacylglycerol molecules within the lattice resulted from its less stable crystal structure (Lawler and Dimick, 2008; Yang and Ciftci, 2016). Figure 3.8. reveals that the addition of low moisture butter to fractionated palm oil affected the polymorphism of the solid lipid particles. The polymorphic forms are characterized by short spacings (d) obtained from X-ray diffraction (XRD) patterns, which was defined as the distance

due to lateral packing of the fatty acid chains on the triacyglycerol molecules (ten Grotenhuis et al., 1999). The short spacings of 0.46 nm, 0.37 nm, and 0.38 nm indicated that fractionated palm oil being β and β' crystalline structures, whereas butter addition resulted in primarily α (d= 0.41 nm) form. After particle formation process, solid lipid particles of fractionated palm oil still exhibited β and β' forms but with reduced intensity. Both observations indicated that the solid lipid particles were less ordered in crystalline structure than the original bulky oil, which is supported by the DSC melting curves (Fig. 3.7.). In solid lipid particles generated from blends of fractionated palm oil and butter, the distribution of α, β, and β' polymorphic forms appeared to be quite similar to the particles obtained from fractionated palm oil but with slight further decrease of β form intensity. This was due to the introduction of butter with relatively lower melting temperature to the mixture, therefore contributing to the less stability of the crystalline structure in the solid lipid particles. The solid lipid particles obtained in this study are hollow and dense-packed, which can be the advantages to develop low calorie, easy-to-use butter ingredients/foods without the need for refrigeration.

3.5. Conclusions

This study demonstrates that nonchemically modified lipids can be used to form hollow microparticles, and possibly nanoparticles, via rapid depressurization of a CO_2-expanded lipid. Lower melting fats with desirable characteristics such as butter for its flavor can be blended with higher melting lipids to be incorporated into the particles. The reported process reduced the density of the particles 5 folds compared to that of the raw solid fats, decreased the melting point, and increased the surface area due to microparticle formation. There are a number of potential unique, beneficial applications of the obtained hollow solid lipid particles. Free-flowing particles enables easier handling of solid fat materials. These particles could also allow solid fats to be incorporated

uniformly into foods. Compared to many common forms of solid fat, the particles created in this study have a much higher ratio of surface area to mass due to their hollow nature and small size. When incorporated into foods, the increased surface area could allow for additional oil coating on the palate so less material could be used while still achieving the same oil mouthfeel, which could be especially valuable in reduced fat and calorie foods. The increased ratio of surface area to mass contributes to quicker melting when the particles are in contact with a heat source as well. This attribute could potentially allow for consumed fats to melt quicker on the palate which could help to reduce the undesirable fatty mouth coating that occurs when lipids with high melting points are consumed and stay in their solid state. These properties could also be applied as unique functional benefits in certain types of foods. For example, the particles could be used in a drink mix powder that is stirred into a warm liquid. The high ratio of surface area to mass allows the particles to have additional contact with the liquid causing quicker melting and mix in.

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Table 3.1. Density of the fractionated palm oil and its blends with low moisture butter, and of the solid lipid particles obtained at different lipid levels.

	Bulk density (kg/m^3)[a]
Fractionated palm oil particles	169.2 ± 4.2
75% fractionated palm oil particles	143.2 ± 7.3
50% fractionated palm oil particles	141.7 ± 3.2
Fractionated palm oil	866.0 ± 63.2
75% fractionated palm oil blend	866.6 ± 58.8
50% fractionated palm oil blend	880.3 ± 70.9

[a] Mean ± standard deviation, n=3.

Table 3.2. Composition of the major fatty acids (%) of low moisture butter, fractionated palm oil (FPO), their physical blends[a], and the obtained particles[b].

Composition	Butter	FPO	FPO-P	75% FPO	75% FPO-P	50% FPO	50% FPO-P
Caproic acid (6:0)	2.4	0.0	0.0	0.5	0.5	1.1	1.0
Caprylic acid (8:0)	1.3	0.0	0.0	0.3	0.3	0.6	0.6
Capric acid (10:0)	3.1	0.0	0.0	0.7	0.7	1.5	1.4
Lauric acid (12:0)	3.5	0.2	0.2	1.0	1.0	1.8	1.7
Myristic acid (14:0)	11.3	1.3	1.3	3.6	3.5	6.2	5.7
Myristoleic acid (14:1)	1.4	0.0	0.0	0.3	0.2	0.7	0.6
Palmitic acid (16:0)	31.1	77.8	78.7	68.2	68.3	55.7	57.9
Palmitoleic acid (16:1)	2.1	0.0	0.0	0.5	0.5	1.0	0.9
Stearic acid (18:0)	10.8	5.0	5.0	6.2	6.4	7.8	7.5
Oleic acid (18:1, n-9)	21.4	12.3	11.6	13.7	12.7	16.4	14.1
Vaccenic acid (18:1, trans)	2.1	0.0	0.0	0.0	0.0	1.2	0.0
Linoleic acid (18:2, n-6)	3.2	2.3	2.1	2.4	2.3	2.7	2.3
SFA	54.6	75.9	78.5	71.3	73.8	65.7	70.3
MUFA	22.0	11.1	10.8	13.0	12.8	16.4	15.3
PUFA	3.4	2.1	2.0	2.2	2.1	2.7	2.2

[a] 75% FPO: 75% fractionated palm oil, 25% butter; 50% FPO: 50% fractionated palm oil, 50% butter.

[b] FPO-P: 100% fractionated palm oil; 75% FPO-P: 75% fractionated palm oil, 25% butter; 50% FPO-P: 50% fractionated palm oil, 50% butter; SFA: Saturated fatty acids; MUFA: Monounsaturated fatty acids; PUFA: Polyunsaturated fatty acids.

Figure captions

Fig. 3.1. Melting behavior of the fractionated palm oil and low moisture butter in the pressurized CO_2.

Fig. 3.2. SEM images of the solid lipid particles obtained at different lipid levels: a, d) 100% fractionated palm oil; b, e) 75% fractionated palm oil, 25% butter; and c, f) 50% fractionated palm oil, 50% butter.

Fig. 3.3. SEM images of the freeze-fractured solid lipid particles: (a, b, c) 100% fractionated palm oil; (d) 75% fractionated palm oil, 25% butter; and (e) 50% fractionated palm oil, 50% butter.

Fig. 3.4. 3D AFM images of the surface topography of the obtained palm-butter microparticles. (a) 100% fractionated palm oil; (b) 75% fractionated palm oil, 25% butter; and (c) 50% fractionated palm oil, 50% butter.

Fig. 3.5. Confocal fluorescence microscopy z-series scanning images of the solid lipid particles. a) fractionated palm oil; b) 25% butter; c) 50% butter.

Fig. 3.6. Particle size distribution of the solid lipid particles: a) fractionated palm oil; b) 25% butter; and c) 50% butter.

Fig. 3.7. DSC melting curves of the solid lipid particles obtained from the blends of fractionated palm oil and low moisture butter.

Fig. 3.8. XRD patterns of the solid lipid particles obtained from the blends of fractionated palm oil and low moisture butter.

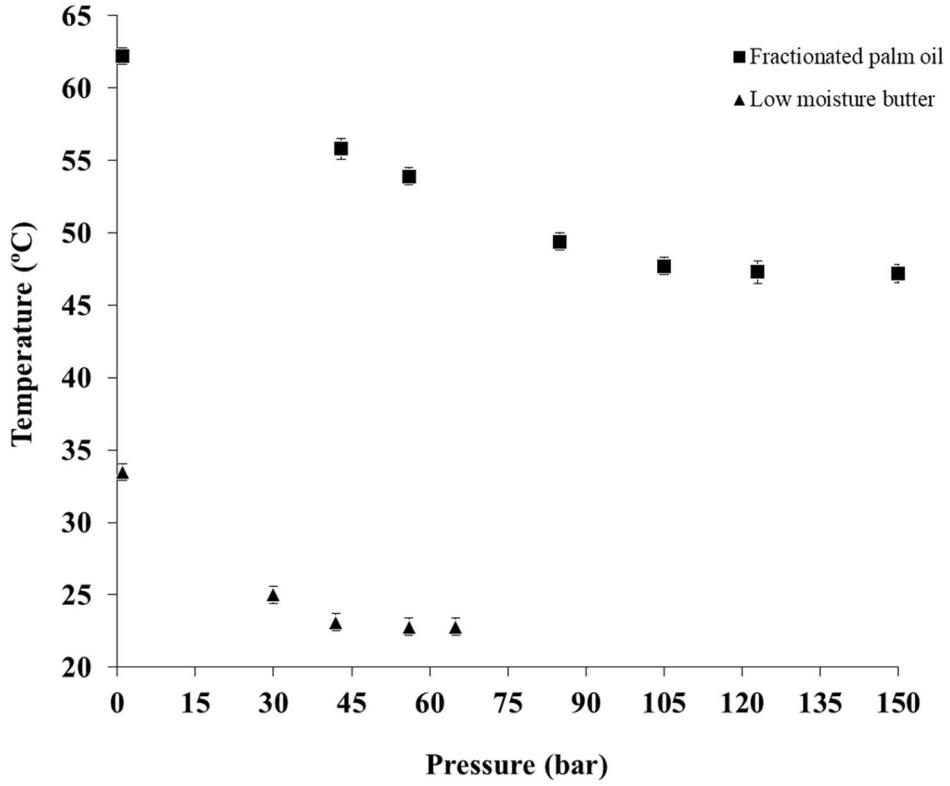
Fractionated palm oil
Low moisture butter
Temperature (°C)
Pressure (bar)
65
60
55
50
45
40
35
30
25
20
0
15
30
45
60
75
90
105
120
135
150

Figure 3.1.

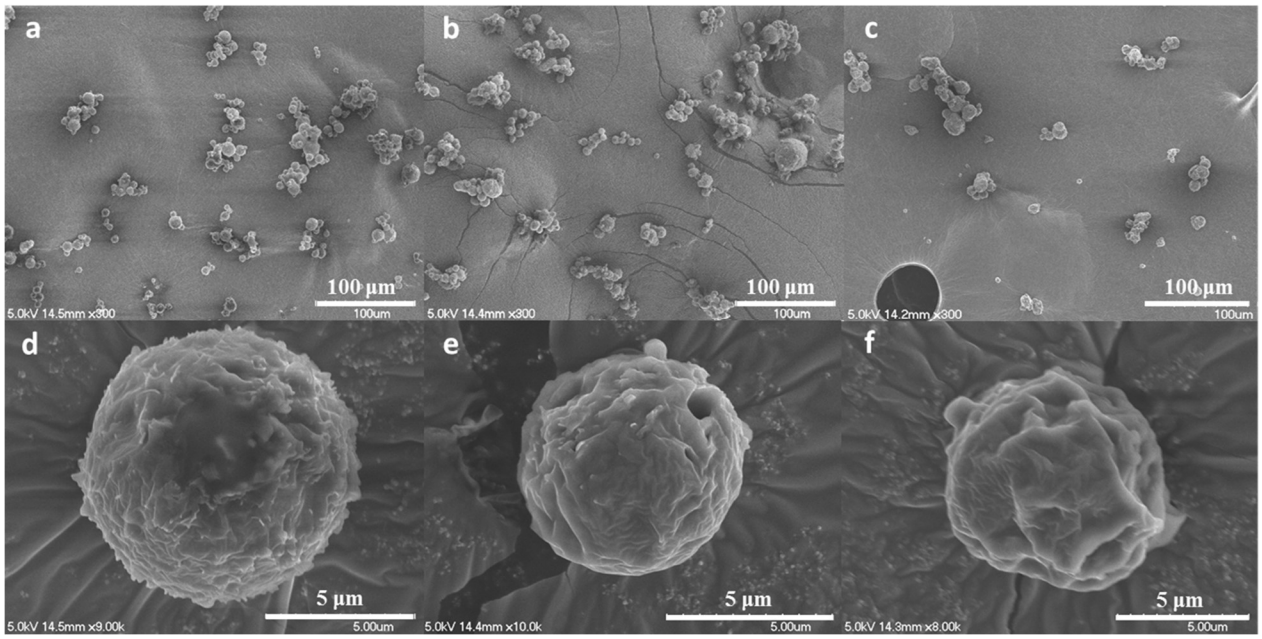
a
100 µm
5.0kV 14.5mm x300
100um
b
100 µm
5.0kV 14.4mm x300
100um
c
100 µm
5.0kV 14.2mm x300
100um
d
5 µm
5.0kV 14.5mm x9.00k
5.00um
e
5 µm
5.0kV 14.4mm x10.0k
5.00um
f
5 µm
5.0kV 14.3mm x8.00k
5.00um

Figure 3.2.

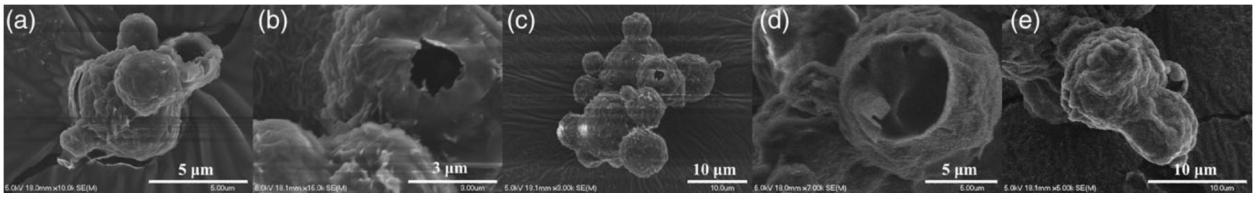

Figure 3.3.

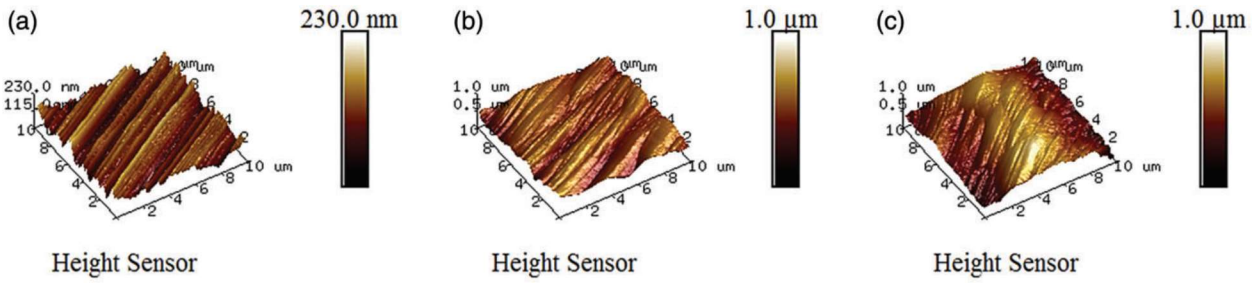
(a)
230.0 nm
230.0 nm
115.0 nm
10 um
(b)
1.0 um
1.0 um
0.5 um
10 um
(c)
1.0 um
1.0 um
0.5 um
10 um
Height Sensor
Height Sensor
Height Sensor

Figure 3.4.

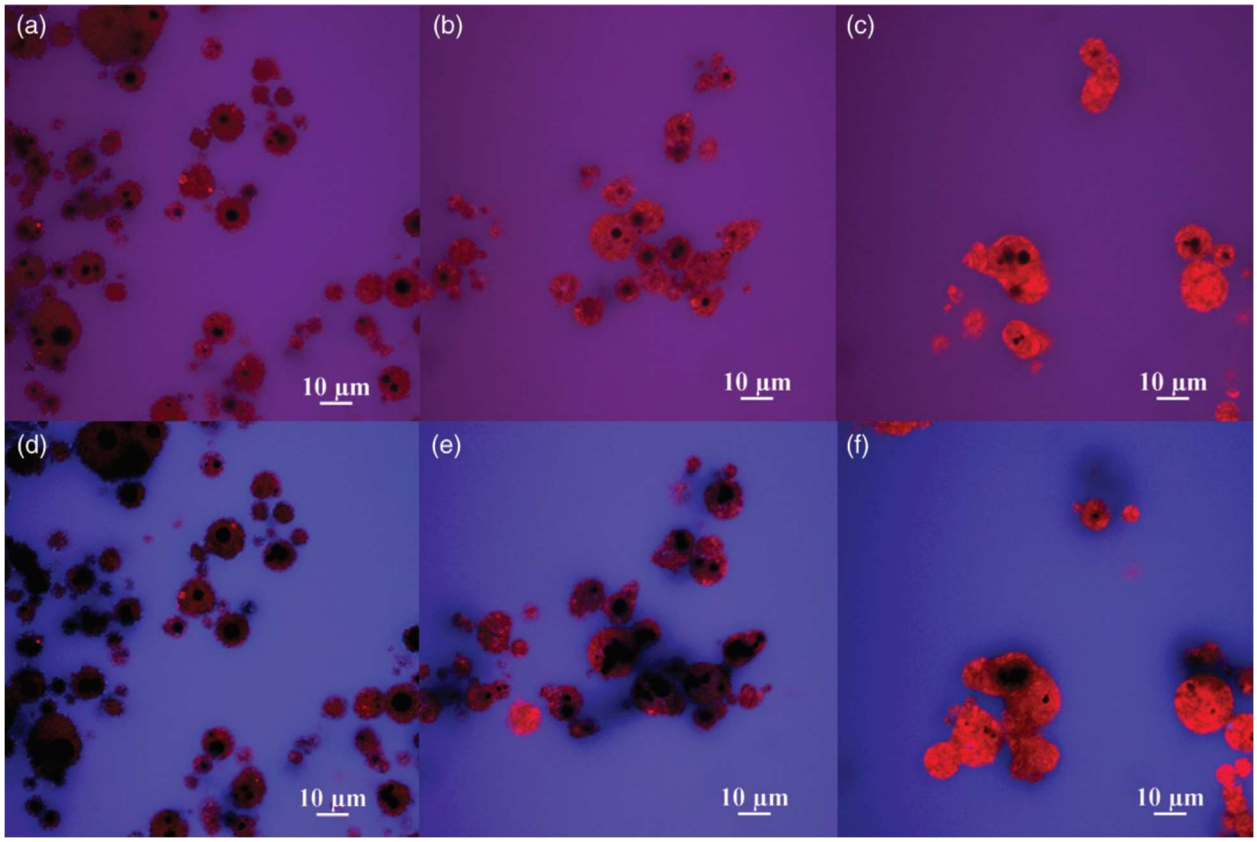

Fig. 3.6.

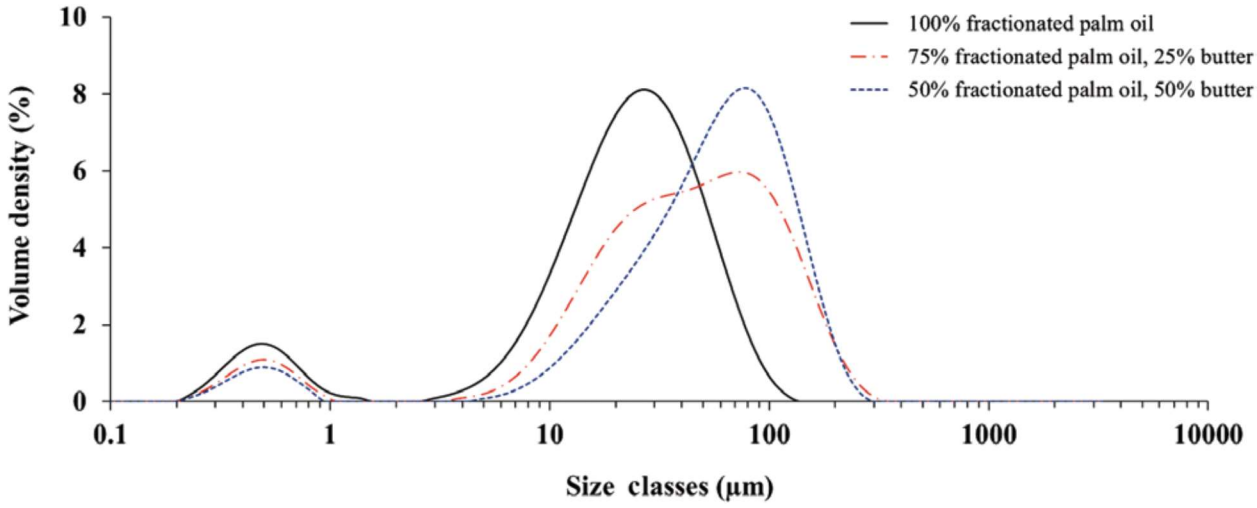
100% fractionated palm oil
75% fractionated palm oil, 25% butter
50% fractionated palm oil, 50% butter
Volume density (%)
Size classes (µm)
0
2
4
6
8
10
0.1
1
10
100
1000
10000

Figure 3.6.

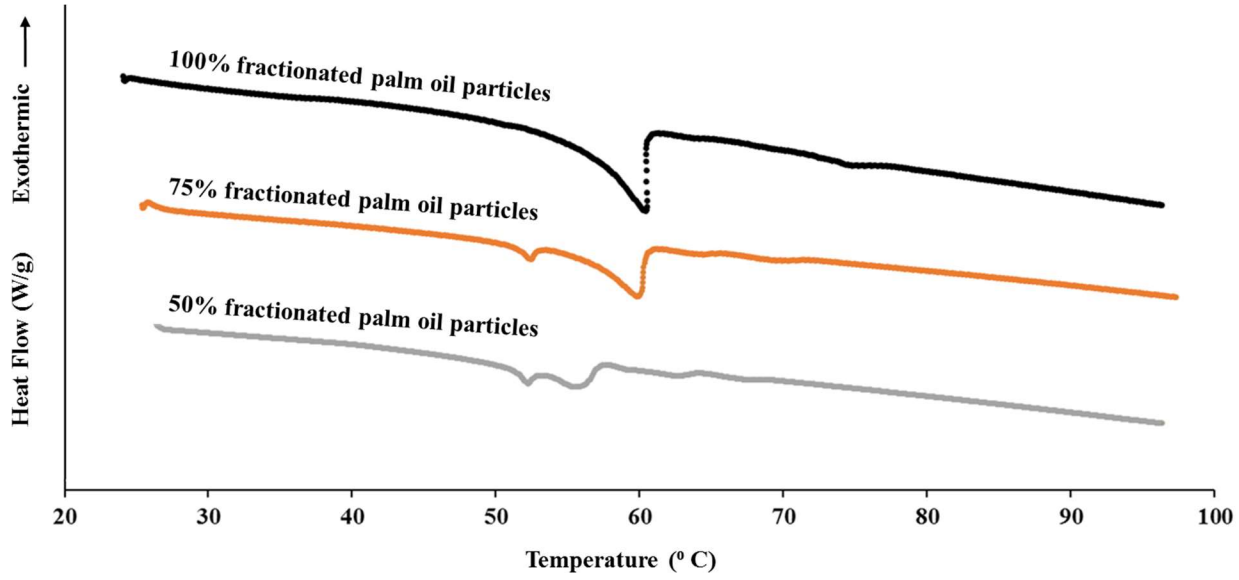
Exothermic
Heat Flow (W/g)
100% fractionated palm oil particles
75% fractionated palm oil particles
50% fractionated palm oil particles
20
30
40
50
60
70
80
90
100
Temperature (° C)

Figure 3.7.

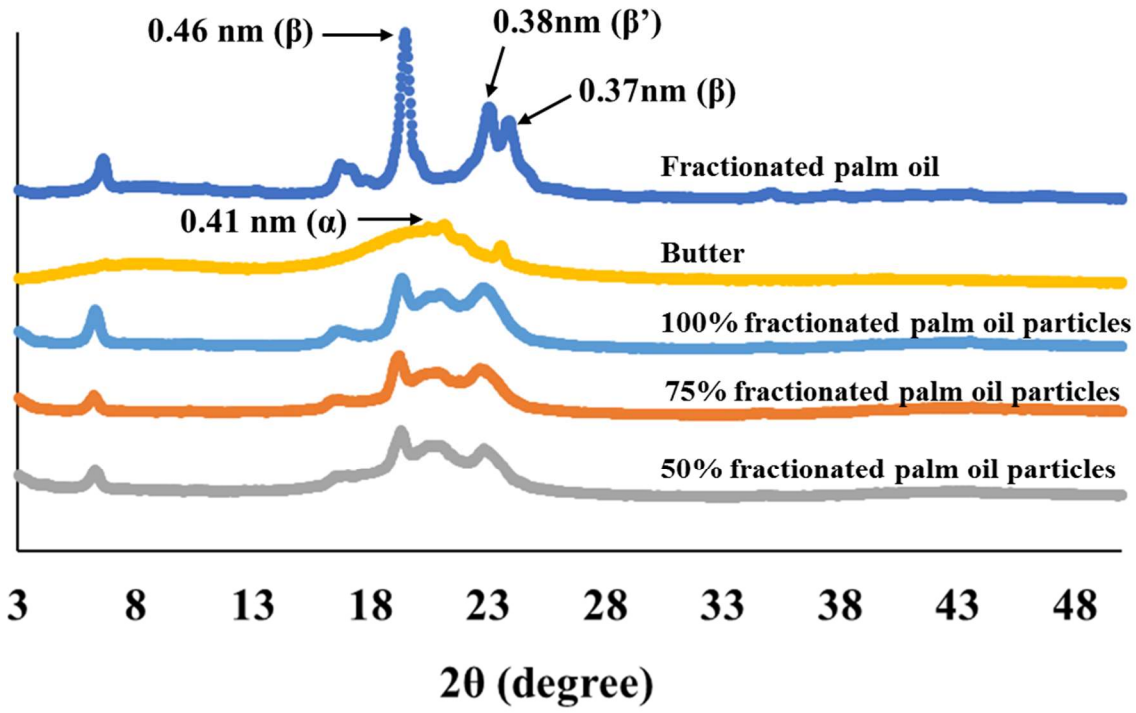
0.46 nm (β)
0.38nm (β')
0.37nm (β)
Fractionated palm oil
0.41 nm (α)
Butter
100% fractionated palm oil particles
75% fractionated palm oil particles
50% fractionated palm oil particles
3
8
13
18
23
28
33
38
43
48
2θ (degree)

Figure 3.8.

CHAPTER 4. PREPARATION OF PASTRIES WITH SHORTENING COMPOSED OF HOLLOW SOLID MICROPARTICLES FROM FRACTIONATED PALM OIL

4.1. Abstract

Solid fats are important components in pastries and help to provide high quality texture and mouthfeel in the finished product. However, these solid fats can be difficult to properly incorporated into pastry dough and add relatively high calorie contributions. The objective of this study was to examine the functionality of free-flowing and low-density hollow microparticles composed of fractionated palm oil when used as the shortening in pasties. Biscuits, puff pastries, and pie crusts were prepared with the lipid microparticles and the quality of the finished products was compared with their counterparts prepared with traditional shortenings including butter, vegetable shortening, and lard. Relative to these traditional shortenings, the pastries made using particle-containing shortenings had a firmer texture. The particle-containing preparation resulted in an additional pastry lift in the biscuits and puff pastries. When shortening levels were reduced, firmer pastry textures and increased lift were observed. Although the reduced shortening levels produced less desirable and firmer pastries in these applications, the lipid microparticles' high ratio of surface area to mass could be potentially beneficial in food applications where reduced oil and calories are sought. Moreover, handling and incorporation of the lipid microparticles are easier than traditional shortenings. The small particle size and free-flowing nature of the lipid microparticles allow for simple weighing and uniform incorporation into the pastry doughs without the need to melt or cut the solid fats into small pieces. In industrial food production, these attributes of the particles could allow for improved large-scale handling and incorporation into pasty formulas, as well as use in continuous production systems.

Keywords: Pastry; Shortening; Lipid; Microparticles; Supercritical CO_2

4.2. Introduction

Solid fats play a critical role in the preparation and finished product quality of baked pastries. The solid fats in pastries help to create a desirable flaky texture after baking, and this functionality is provided by the fats interrupting the gluten matrix that forms in dough made with the flour from wheat or other cereal grains (Knightly, 1981; Baker and Mize, 1942; Baldwin et al., 1963; Harvey, 1937). Gluten proteins in the flour form the dough and give the dough strength and elasticity (Hirahara and Simpson, 1961). Although gluten is a required ingredient in many pastries, overdevelopment of gluten can create undesirable textures that are too firm or chewy. A properly shortened pastry is expected to be crumbly and has a soft, flaky texture. Shortenings are able to interfere with the formation of the gluten strands in dough leading to a "shorter", less elastic dough development (Finney et al., 1987; Souza et al., 1994; Lowe et al., 1938).

Although these solid fats are critical to the quality of pastries, their use can present various challenges. Storage and handling of solid fats can be difficult because they are often packaged in large containers, which in turn requires heavy equipment to transport solid fats to batching areas and need further procedures before incorporation into a recipe. Cutting and melting solid fats are often required before being added to an ingredient-batch mixture, which are time-consuming and can cause preparation inefficiencies. In addition, maintaining a high temperature that is above the melting point of solid fats requires costly energy and can also promote oil degradation. Moreover, there are a few solid fat challenges unique to baked foods such as pastries. First, if the shortening is not uniformly distributed into the dough, the texture and appearance will present inconsistencies in the finished baked product. Second, compared to other macronutrients, fat contribution of nine calories per gram is relatively high. Therefore, the functionality of fat as a shortening in baked foods would make them nutritionally high in fat and calories. To reduce fat content and caloric

value of baked foods, it is plausible to reduce shortening usage from formulations by increasing the amount of proteins, carbohydrates, fibers, and water. However, fat substitution in a such formulations is not easy. A potential solution to the above-mentioned challenges is to use hollow solid lipid microparticles that are light, free-flowing, quick to remelt, and easy to be properly distributed into the dough to replace part of traditional shortenings.

In the recent decade, studies demonstrated that supercritical carbon dioxide (SC-CO_2) technology has been a promising method to form solid lipid microparticles (Gudeman et al., 2019; Yang and Ciftci, 2016; Lubary et al., 2011; García-González et al., 2010; Mandžuka and Knez, 2008; Sampaio de Sousa et al., 2007; Bertucco et al., 2007). Micron size solid lipid particles can be generated via gas-saturated solutions (PGSS), gas-assisted melting atomization (GAMA), supercritical melt micronization, or atomization of the CO_2-expanded lipids. Recently, Gudeman et al. (2019) reported formation of low-density and free-flowing hollow solid lipid microparticles from fractionated palm oil and butter mixture using SC-CO_2. In this process, natural cooling around the nozzle and surrounding area caused by the Joule-Thomson effect allowed for solidification of the liquid lipid bubble resulted from CO_2 expansion during depressurization. The obtained hollow solid lipid microparticles are easy to handle and be incorporated into foods with improved food quality. Moreover, the small particle size and hollow nature contribute to a high ratio of surface area to mass which could allow for reduced fat usage while still functioning to interrupt the gluten matrix of the baked product. However, to the best of our knowledge, the performance of hollow solid lipid microparticles as shortening fat in baked pastries has not yet been assessed.

The three pastry types tested in this study were chosen based on the multiple unique functionalities of shortenings in each. Biscuits have shortening incorporated throughout with rising

caused by synthetic leavening agents. An ideal biscuit should have a tender and flaky texture . Puff pastries have shortening distributed in layers with rising. An ideal puff pastry should have distinct, laminated layers with a flaky texture. Finally, pie crusts have shortening uniformly distributed without rising, and an ideal pie crust should be thin with a flaky texture.

Therefore, the primary objective of this study was to investigate the feasibility and potential benefits of preparing pastries with free-flowing and low-density shortening fat composed of hollow solid palm oil microparticles obtained by SC-CO_2 versus standard butter, lard, and vegetable shortenings. Specific objectives were to: (i) make biscuits, puff pastries, and pie crusts using various shortening types and usage levels; and (ii) characterize the qualities of finished baked pastries including pastry dimensions, peak force hardness, fracturability, and appearance (aesthetics).

4.3. Materials and Methods

4.3.1. Materials

Fractionated palm oil was acquired from Bunge Loders Croklaan (Channahon, IL, USA). CO_2 (dry, 99.99% purity) was obtained from Matheson (Lincoln, NE, USA). Control shortenings were all purchased from a local grocery store (Omaha, NE, USA). The lard was Armour brand Premium All Natural Lard (UPC code 5258500715). The vegetable shortening was Crisco brand All-Vegetable Shortening (UPC code 5150024234). The butter was Land O Lakes brand Unsalted Butter (UPC code 3450015150).

Additional baking ingredients were also commercially available and purchased from local grocery stores (Omaha, NE, USA). The flour was Gold Medal brand Enriched, Bleached, Presifted All Purpose Flour (UPC code 1600010610). The nonfat dry milk was Nestle brand Carnation

Instant Nonfat Dry Milk (UPC code 5000003322). The salt was Morton brand Salt (UPC code 2460001001). The sugar was C&H brand Confectioners Sugar Powdered Pure Cane Sugar (UPC code 1580007032). The baking soda was Arm & Hammer brand Pure Baking Soda (UPC code 3320001140). The ammonium bicarbonate was Anatoli brand Ammonium Bicarbonate (UPC code 201589021362). The baking powder was Rumford brand Aluminum-Free Baking Powder (UPC code 4161700227).

4.3.2. Production of hollow solid fractioned palm oil microparticles using carbon dioxide

A home-made particle formation system was used to form free-flowing hollow solid lipid microparticles from fractionated palm oil. A detailed description of the system and operating procedure can be found in previously reported publications (Yang and Ciftci, 2016; Gudeman et al., 2019). Briefly, the main components of the particle formation system are two high-pressure syringe pumps, a pre-heating section, a 100 mL high-pressure expansion vessel, a magnetic drive, a depressurization valve, a nozzle and temperature controllers. Temperature of the vessel was set at 48 °C, which was the lowest melting point of the fractionated palm oil in pressurized CO_2 (Gudeman et al., 2019). Our previous study successfully generated smaller ($d_{50\%}$ = 278 nm) hollow spherical particles at 50 μm nozzle diameter and 200 bar (Yang and Ciftci, 2016). Therefore, processing conditions of 50 μm nozzle diameter and 200 bar were used. Temperature of the depressurization valve and nozzle was kept at 130 °C to eliminate freezing and clog of the nozzle due to the Joule-Thomson effect during atomization.

Fractionated palm oil was fully melted at 130 °C, and then 20 mL of the molten sample was carefully injected into the vessel through the sampling port. After injection and sampling port closure, the vessel was gradually pressurized to 200 bar. Then, the molten fractionated palm oil and pressurized CO_2 were mixed using the magnetic drive at 1000 rpm for 1 hour. During mixing,

CO_2 dissolved in the lipid and formed CO_2-expanded lipid. Next, the magnetic drive was turned off and the mixture was allowed to stabilize for 10 minutes. The pressure of the syringe pumps was set at 210 bar (10 bar above the pressure in the vessel), the inlet valve was opened followed by immediate opening of the depressurization valve, resulting in atomization of the CO_2-expanded lipid through the nozzle. The solid lipid particles were generated and finally collected in the sample collection vessel.

4.3.3. Pastry preparation procedures

4.3.3.1. Biscuit

The biscuit preparation procedure was adapted from Gupta and Tiwari (2014)The ingredients and usage levels are listed in Table 4.1. Sugar and fat were added to a KitchenAid mixer (Model No. K5SS). The blend was creamed by mixing for 2 minutes. Flour, nonfat dry milk, and baking powder were then added to the mixer. Salt, ammonium bicarbonate, and sodium bicarbonate were firstly mixed with water, and the aqueous solution was subsequently added to the mixer. With all the added ingredients, the blend was mixed for an additional 2 minutes to form a soft dough. The dough was removed from the bowl and kneaded on a flat surface to obtain a uniform mix. Then the kneaded dough was rolled to a uniform thickness of 2.5 cm and cut into 5 cm circles to form the biscuits. The biscuits were then transferred onto a cookie sheet on a baking tray. Baking was carried out at 200 °C for 9 minutes in a conventional oven.

4.3.3.2. Puff pastry

The puff pastry preparation procedure was adapted from Gerrard et. al. (2000). The ingredients and usage levels are listed in Table 4.1. All shortening types were placed in a -20 °C freezer for 1 hour prior to use. Flour and salt were added in a KitchenAid mixer (Model No. K5SS)

and mixed for 15 seconds. Water was then added and mixed for 1 minute. The formed dough was rolled to a uniform thickness of 3 cm. Then the shortening was folded into the dough with two folds and rolled again to reduce the thickness to 3 cm. The dough was placed in a sealed plastic bag and frozen at -20 °C for 15 minutes. The dough was then folded in fourth and rolled to reduce the thickness to 1 cm. This procedure of folding the dough four times, rolling it, and freezing for 15 minutes was repeated two additional times. The pastry was then cut into 5 cm circles and allowed to rest for 30 minutes at room temperature (21 °C). Then, the pastries were transferred onto a baking sheet on a baking tray. Baking was carried out at 230 °C for 10 minutes in a conventional oven.

4.3.3.3. Pie crust

The pie crust preparation procedure was adapted from Berglund and Hertsgaard (1986). The ingredients and usage levels are list in Table 4.1. The flour was sifted, and shortening was cut and mixed into the flour with a pastry blender until the shortening was pea sized. The mixture was then added to a food processor (Model No. FPSTHB26RDP-0002SPD, Oster Sunbeam Products Inc., Boca Raton, FL, USA). Water was added to the mixture, and the food processor was pulsed on low for 1 second and repeated 5 times. A dough ball was formed, placed between 2 sheets of plastic wrap, and flattened to a uniform thickness of 4 mm between two pans. The dough crust was then cut into 5 cm squares and baked in a conventional oven at 220 °C for 10 minutes.

4.3.4. Determination of pastry dimensions

Dimensions of the pastries were determined with a digital caliper (Pittsburgh, 12”, model No. 47261). Before baking, the horizontal side length and vertical height (T_0) of each pastry variable was measured. After baking, the widest and narrowest horizontal portions as well as the tallest and shortest vertical portions of the pastry were measured. All of these measurements were

performed on three samples for each set of variables. The diameter (D) and thickness (T) of the pastry after baking were calculated by averaging the widest and narrowest side widths, and the tallest and shortest heights, respectively. The average value for each dimension was reported in millimeter. The pastry lift (T/T_0) was calculated as the ratio between the average baked height (T) and the dough height before baking (T_0).

4.3.5. Texture analysis of pastries

Hardness and fracturability analysis of the pastries were determined using a TA-XT Plus texture analyzer (Model No. 5014, Stable Micro Systems Ltd., Godalming, England) equipped with a 3-point bending rig (HDP/3PB) and a heavy-duty platform (HDP/90). The span between the two supports was 30 mm. The upper blade was attached to equally split the distance between the two supports. The protocol was adapted from the application study for the measurement of hardness and resistance of buscuits/cookies to bend or snap (Stable Micro Systems Ltd., 2008). The texture analyzer settings were: pre-test speed at 1.0 mm/s, test speed at 3.0 mm/s, post-test speed at 10.0 mm/s, distance at 50 mm, trigger force at 50 g, and data acquisition rate at 500 pps. The sample was then set centrally on top of the two bottom supports. The maximum force (g) and the distance (mm) to break off the sample were recorded. The maximum force (g) indicated the hardness of the pastry and the distance (mm) from the trigger force to the sample breaking referred to pastry fracturability.

4.3.6. Qualitative characterization of pastry structure and aesthetics

Photographs of the baked pastries were taken in the controlled setting of a BestLight® Studio photography box. Images were taken from the top, bottom, and side of each pastry. Each pastry was then sliced in half and a cross-sectional photograph was taken to characterize its air cells, lamination layers, and structural uniformity.

4.3.7. Statistical analysis

Data are presented as mean ± standard deviation based on triplicate experiments and analyses. A single factor ANOVA was used to analyze differences in dimensions, peak force hardness, and fracturability among shortening types for each type of pastry. SAS version 9.3 was the statistical software package used for all analyses (SAS Institute Inc., NC, USA). An alpha level of <0.05 was used to denote significance. Post hoc test was conducted by using Tukey's multiple comparison.

4.4. Results and Discussion

4.4.1. Characterization of the hollow solid microparticles from fractionated palm oil

Hollow solid lipid microparticles from fractionated palm oil were successfully obtained by atomization of the CO_2-expanded lipid. Figure 4.1. shows the particle morphology of the hollow solid lipid microparticles (Gudeman et al., 2019). The obtained particles were spherical, intact, and free flowing. During mixing of CO_2 and fractionated palm oil, CO_2 dissolved in the lipid and the lipid expanded at the bottom of the high-pressure expansion vessel. This CO_2-expanded lipid phase was responsible for the atomization at the nozzle upon depressurization. When the CO_2-expanded lipid was atomized, a liquid droplet of fractionated palm oil and CO_2 mixture was formed and then this droplet turned into a liquid lipid bubble due to expansion of the dissolved CO_2 at atmospheric pressure (Yang and Ciftci, 2016). At the same time, temperature of the atomized particles suddenly decreased due to Joule-Thomson effect (Yang and Ciftci, 2016). Upon cooling, the liquid lipid bubble solidified and formed hollow solid lipid microparticles. Figure 4.1. (a, c, d) illustrated spherical shape of the fractionated palm oil particles, and Figure 4.1. (b, c, d) showed hollow structure of the particles. Gudeman et al. (2019) previously reported that the bulk density of the fractionated palm oil particles was reduced to 169 kg m^{-3} as compared to the original lipid

(866 kg m^{-3}) before particle formation. The decrease in density was caused by the hollow structure and small particles size as well as the packing spaces among the particles (Gudeman et al., 2019). The major melting peak temperature significantly decreased from 67.7 °C to 61.0 °C after particle formation ($p<0.05$), which was attributed to the small particle size, hollow structure within a thin shell and polymorphic form transition from β and β' to α (Gudeman et al., 2019).

4.4.2. Pastry dimensions

4.4.2.1. Biscuit

The effects of shortenings on biscuit dimension were displayed in Table 4.2. The diameter of biscuits were overall similar among the shortening types except the one obtained with 50% lard reduction. Biscuits prepared using butter had the greatest diameter (45.1 mm) and 50% lard reduction had the least (41.8 mm) ($p<0.05$). The decrease in biscuit diameter for 50% lard reduction among others was due to the increased elastic properties of dough, consequently resulted in less lateral expansion during baking (Hadnađev et al., 2015). The traditional shortening types did not appear to have a major impact on the thickness of biscuits ($p>0.05$), whereas biscuits prepared using fractionated palm oil microparticles significantly increased the thickness ($p<0.05$). In addition, the shortening types had more pronounced impacts on biscuit thickness and in turn, affected pastry lift. Biscuits prepared using fractionated palm oil particles instead of traditional shortenings (both in original and 50% oil reduction) achieved the highest lift (4.1 and 3.8), followed by lard (3.3) and 50% lard reduction (3.0), with Crisco (2.8) and butter (2.6) being the lowest ($p<0.05$). There are a few potential explanations for the significantly higher pastry lift occurred in biscuits with fractionated palm oil particles. Firstly, the small particle size of the fractionated palm oil particles increased contacting surface area with other ingredients, hollow nature due to CO_2 expansion upon atomization decreased the packing spaces among the particles

and the dissolved CO_2 was released when the particles melted during baking. The released CO_2 pockets were able to produce the additional rise in the biscuits. Secondly, the fractionated palm oil particles did not interrupt the gluten matrix of the dough as much as the traditional shortenings. Therefore, the more established gluten matrices in the dough prepared using fractionated palm oil particles were then able to better capture the air released from the leavening ingredients and contributed to more lift in the biscuits. This statement was supported by Figure 4.2. where the high peak hardness of the biscuits prepared using fractionated palm oil particles was higher than the other formulations using traditional shortenings. Thirdly, solid fats were able to fill gaps in the gluten matrix while enhancing gas retention (Baker and Mize, 1942; Baldwin et al, 1963; Baldwin et al, 1965). In particular, the small particle size and large quantity of particles allowed them to effectively fill gaps in the dough and prevented gas from escaping.

4.4.2.2. Puff pastry

The dimensions of the puff pastries prepared from traditional shortenings or fractionated palm oil particles were shown in Table 4.3. Puff pastries prepared using lard had the greatest diameter (47.0 mm) while butter exhibited the least (44.8 mm) ($p<0.05$). There were significant differences in the thickness of the puff pastries prepared using different shortenings ($p<0.05$). The highest thickness was observed for the puff pastries obtained with fractionated palm oil particles (both in original or in 50% reduction) and butter, which was more than twice the thickness from the pastries from lard ($p<0.05$). In this case, without the presence of synthetic leavening agents in the formula, the marked rising indicative as thickness and pastry lift was due to the components inherent to the shortening itself. The moisture in butter was released as steam during baking and contributed to the rise of the puff pastries. Similar to biscuits, the hollow structure of the particles in the puff pastries released the entrapped CO_2 resulted from expansion when heated during

baking, and therefore leading to the rise in the pastries. On the other hand, the fractionated palm oil particles may have also filled potential gaps in the dough to better retain any gases present. The puff pastries that had much lower thickness and pastry lift were those obtained from lard and Crisco, all of which had minimal moisture, trapped air inherent to themselves, and surface area to fulfill potential gaps in the dough.

4.4.2.3. Pie crust

The dimensions of the pie crusts prepared from traditional shortenings or fractionated palm oil particles were presented in Table 4.4. The diameter of pie crusts were overall similar among the shortening types, ranging from 46.4 to 50.9 mm ($p>0.05$).There were significant differences in the thickness of the pie crusts prepared using different shortenings ($p<0.05$). The highest thickness (11.6 and 10.6 mm) was observed for the pie crusts obtained with fractionated palm oil particles (both in original or in 50% reduction), whereas those using traditional shortenings exhibited similar thickness between 7.9 and 10.1 mm. Since the pie crust formula did not contain synthetic leavening agents, variations in the thickness of the pie crusts prepared using different shortenings would likely be inherent to the shortenings themselves, which was similar to the puff pastries. These results correlated well with the peak hardness of the pie crusts (Fig. 4.6.), with those using lipid particles and 50% lard reduction had the greatest peak hardness. The release of the entrapped gas from the hollow structure of the particles and the potential of the small particles may have filled gaps in the stronger gluten matrices presented at these variables to increase entrapment of gases released during baking were attributed to the increased thickness and lift.

4.4.3. Texture analysis of the pastries

4.4.3.1. Biscuit

The texture properties are one of the most important quality parameters of pastry products. The hardness was determined by the peak force required to break the biscuit. The fracturability measures the ability of biscuit to fight to retain its original status or form and was recorded as the distance from the initial trigger force of the texture analyzer to where the sample broke. Pastries with lower hardness levels and increased fracturability are generally considered to have a more desirable texture and mouthfeel. These measurements are helpful to indicate the quality of the pastry shortening in its role of interrupting gluten matrices. The results from texture analysis of biscuits were displayed in Figure 4.2. and 4.3. The results showed that biscuits made of fractionated palm oil particles (both in original or 50% oil reduction) and 50% lard reduction had the highest breaking force and were significantly different ($p<0.05$) from biscuits containing butter, Crisco, and lard (Fig. 4.2.). The measurements of the breaking strength revealed that the biscuits with fractionated palm oil particles and lower fat content expressed higher breaking strength values, i.e., they were harder compared to other samples using a higher fat content of the traditional shortenings. Previously, it was reported by Mamat and Hill (2014) that the biscuits prepared with palm mid-fraction, which contained a relatively higher solid fat oil, had higher breaking force as compared to the counterparts by using palm oil and palm olein. In addition, Jacob and Leelavathi (2007), Goldstein and Seetharaman (2011), and Hadnađev et al. (2015) showed similar relationship between breaking force and shortening oil usage level; less oil usage led to greater hardness of bakery product. Two likely contributing factors can explain for the increased biscuit hardness. Firstly, the increased hardness of biscuits prepared from fractionated palm oil particles at both levels could be due to the particles were not as effective as the traditional shortenings to interrupt the gluten matrix in its shortening and aerating roles. According to Manley (2000), during mixing in biscuit production, the fat compound and the aqueous phase compete for

the surface of flour. If the fat coats the flour before it is hydrated, the gluten network is interrupted, and a shorter less-hard biscuit is produced after baking. Therefore, the biscuits made of fractionated palm oil particles were not as competitive as water to attach on the flour; the gluten strands may be able to simply form around the particles, leaving the particles with minimal impact on the matrix and consequently a more extensive gluten network was formed leading to harder biscuits. Secondly, the reduced shortening oil level to 50% in both lard and fractionated palm oil particles lowered the ratio of the shortening to the gluten containing flour, therefore, the oil was less able to interrupt the formation of the gluten matrices and less quantities of air can be retained during baking resulting in harder texture compared to higher shortening content (Hadnađev et al., 2015). Moreover, these results agreed with the values of thickness and lift (Table 4.2.); biscuits with higher thickness and lift were also characterized by higher breaking strength values. Similar findings were previously reported by Hadnađev et al. (2015).The height of the curves shown in Figure 3 was directly correlated with the peak force (hardness) in Figure 4.2., and the distance (in x- axis) shown in Figure 4.3. illustrated the fracturability of the sample, which was summarized in Table 4.5. The biscuits prepared from fractionated palm oil particles at 50% oil reduction required the furthest distance to be broken ($p<0.05$) indicating reduced fracturability relative to other samples (Table 4.5.). The decreased oil level and presence of small particles did not interrupt the gluten matrix as effective as the traditional shortenings, which resulted in an intact product elasticity.

4.4.3.2. Puff pastry

The results from texture analysis of puff pastries were presented in Figure 4.4. and 4.5. The results showed that puff pastries made of fractionated palm oil particles (both in original or 50% oil reduction) and 50% lard reduction had the highest breaking force (Fig. 4.4.). Similar to the

observations in biscuits, the fractionated palm oil particles and reduced oil level are likely contributing factors to the increased hardness of the puff pastries. Previously, Garcia-Macias et al. (2011) reported the performance of palm-based fat blends in puff pastries. They demonstrated that the palm-based fat blends with low saturated fat content melted quickly, thus prevented puffing in the pastry and the hardness and lift of the product increased and decreased, respectively, as compared to butter. In contrast to their observation, although had similar hardness, the small particle size and hollow nature of the fractionated palm oil particles allowed to trap a larger quantity of air and contributed to a relatively higher thickness and lift than traditional shortenings and palm-based fat blends. With the exception of the puff pastries prepared from lard, the puff pastries exhibited various small peaks over a longer distance (Fig. 4.5.) relative to the biscuits and pie crusts, which was due to the many individual layers that were formed in the laminated puff pastry dough. These multiple peaks and valleys of each sample likely represented the breaking by the blade of the texture analyzer through the layers of the sample. The narrower curves from the puff pastries containing lard indicated fewer layers and air pockets within the sample, which was also evidenced in the cross-sectional images of the dense puff pastry using lard (Fig. 4.10.) In addition, the lard shortened puff pastries also had significantly increased fracturability relative to the other variables ($p<0.05$). With the trigger force being started at the first layer of the puff pastry, there was an increased distance prior to the sample breaking for the non-lard variables (Table 4.5.).

4.4.3.3. Pie crust

The results from texture analysis of pie crusts were shown in Figure 4.6. and 4.7. The pie crusts made of fractionated palm oil particles at 50% oil reduction had the highest breaking force and were significantly different ($p<0.05$) from the other samples containing butter, Crisco, and lard, whereas samples with fractionated palm oil particles and 50% lard reduction exhibited similar

hardness to that of butter ($p>0.05$) (Fig. 4.6.). As stated previously, the fractionated palm oil particles and reduced oil level are likely contributing factors to the increased hardness of the pie crusts. In addition to the increased hardness, the texture curves of pie crusts made from fractionated palm oil particles (both in original or 50% oil reduction) and 50% lard reduction presented much wider and various peaks than the mostly narrower and singular peaks observed in their counterparts prepared using butter, Crisco, and lard (Fig. 4.7.). As observed in the biscuits and puff pastries, the fractionated palm oil particles and a reduced oil level appeared to provide weaker shortening functionality leading to decreased fracturability. With the gluten matrix less interrupted, additional product elasticity presented and contributed to increased distances to breakage.

4.4.4. Qualitative characterization of pastry structure and aesthetics

4.4.4.1. Biscuit

Images of the obtained biscuits were shown in Figure 4.8.. Visual observation of the biscuits showed well-distributed air cells among all the samples. The top texture of the biscuit made from butter appeared to be noticeably smoother than the other samples which exhibited more wrinkles, possibly due to the distribution of the oil in the dough prior to baking and formation of holes and tunnels through which the gas exited to the outside. In the cross-sectional images, the biscuits prepared using fractionated palm oil particles (both in original or 50% oil reduction) possessed a less dense and open structure with more air pockets between the material layers than the other shortening variables. These air pockets contributed to a relatively higher thickness and pastry lift, which was observed in the pastry dimensions (Table 4.2.). Biscuit dough made of semi-solid fat normally gives better structures during baking than dough made of liquid oil. The crystals in the solid fat portion are separated from the liquid oil during mixing and become enveloped in a protein membrane, which allows solid fat crystals to attach to air bubbles. During baking, the solid

fat crystals melt and the protein membrane is incorporated into the surface of the bubbles with expansion and thus increasing the breaking force (Manley, 2000). In our case, fractionated palm oil particles attached to air bubbles with greater exposure due to small particle size, and the particles consisted of polymorphic form of α, β' and β, which melted at different temperatures to better incorporate the protein membrane into the bubbles' surface and consequently led to higher rise and hardness in the finished product.

4.4.4.2. Puff pastry

Images of the obtained puff pastries were displayed in Figure 4.9. The top texture of the puff pastry made from fractionated palm oil particles appeared to be smoother than the other samples. Browning were seen on the bottom of each pastry, and the one prepared using butter contained the most prominent dark browning. This browning could potentially be a result of the dairy proteins and carbohydrates presented in butter. The increased pastry lift were observed in the side view of the samples, which was consistent with the dimension results (Table 4.3.). In addition, the lamination layers of the puff pastries with fractionated palm oil particles (both in original or 50% oil reduction)were easily noticed in the side view. After cutting the pastries, the large air pockets and lamination layers of the samples with butter and fractionated palm oil particles (both in original or 50% oil reduction)were prominently displayed. The air pockets in the puff pastries containing fractionated palm oil particles appeared to be more numerous and uniform than those found with butter. The rest of samples exhibited fewer, smaller air pockets and layers with a more compact, dense appearance. These observations indicated that the fractionated palm oil particles (both in original or 50% oil reduction) were able to make desired puff pastries in distinct, laminated layers with a flaky texture, which was comparable to butter and noticeably better than Crisco and lard.

4.4.4.3. Pie crust

Images of the obtained pie crusts were presented in Figure 4.10. There were no major aesthetic differences among the shortenings from the views from top, bottom, and side. A slightly higher thickness and lift were observed at the sample using fractionated palm oil particles (Fig. 4.10., Table 4.4.). The cross-sectional images showed that pie crusts prepared from fractionated palm oil particles (both in original or 50% oil reduction) had layers that made the sample less dense, which was due to the expansion and release of the trapped gas resulted from melting of the particles during baking. However, the lift was not significant ($p>0.05$) between the pie crusts prepared from fractionated palm oil particles at 50% oil reduction and those by butter, Crisco, and lard (Table 4.4.), suggesting that the fractionated palm oil particles with a reduced oil level has the potential to be used as a natural alternative shortening to make pie crust with minimal rising.

4.5. Conclusions

This study examined the use of hollow solid lipid microparticles as a shortening in pastries in comparison with standard shortenings including butter, Crisco, and lard. The pastries were chosen based on the multiple unique functionalities that shortenings play in each. Biscuits have shortening uniformly distributed throughout with rising, puff pastries have shortening distributed in layers with rising, and pie crusts have shortening distributed uniformly without rising. Compared to the standard shortenings, the fractionated palm oil particles provided additional firmness on the pastries. A possible explanation is that the particles were small in size so that the gluten matrices were able to form around the particles without proper interruption. The larger size of cuts of the standard shortenings allowed them to truly interact with the gluten matrix, therefore, the gluten matrix was weakened and led to a less firm pastry texture. Pastries prepared from fractionated palm oil particles exhibited more lift in the biscuits and puff pastries versus the

standard shortenings. This was likely related to the gluten matrix as well; a more intact gluten matrix was better able to trap the gases that contributed to pastry lift. The small size and uniform distribution of the particles may have also filled gaps in the dough allowing for better retention of released gases. Reduced shortening level were examined for lard as well as the particles. Both pastries exhibited firmer textures and increased lift. Although the particles did not provide strong shortening properties at 50% oil reduction, the high surface area and low-density did hold potential for other applications where reduced oil and calories are desired. In addition, the free-flowing solid lipid particles were easy to handle, allowed for easier pouring and weighing during benchtop production without the need to cut and melt solid fats. Small particle size makes uniform incorporation into the pastry doughs easily. Moving beyond benchtop production scale to commercial levels, hollow solid lipid particles could potentially be used in vibratory or screw feeders for addition and easy food incorporation in continuous systems.

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Table 4.1. Pastry formulations in original or 50% oil reduction (OR).

Ingredients (g)	Biscuit		Puff pastry		Pie crust	
	Original	50% OR	Original	50% OR	Original	50% OR
All purpose flour	64	64	50	50	56	56
Water	28	28	28	28	23	28
Shortening (butter, lard, Crisco, or particles)	16	8	25	12.5	30	15
Powdered sugar	18	18				
Nonfat dry milk	1	1				
Ammonium bicarbonate	0.5	0.5				
Salt	0.4	0.4	0.9	0.9		
Baking powder	0.3	0.3				
Sodium bicarbonate	0.2	0.2				

Table 4.2. Dimensions* of biscuits prepared from traditional shortenings or fractionated palm oil particles.

Shortening type	Diameter (D, mm)	Thickness (T, mm)	Pastry lift (T/T_0)
Butter	45.1 ± 0.1 a	6.6 ± 0.3 b	2.6 ± 0.1 c
Crisco	44.3 ± 0.4 ab	7.0 ± 0.4 b	2.8 ± 0.2 c
Lard	44.4 ± 1.2 ab	8.3 ± 0.8 b	3.3 ± 0.3 bc
Lard: 50% oil reduction	41.8 ± 0.6 c	7.5 ± 0.1 b	3.0 ± 0.3 bc
Particles	44.2 ± 0.4 ab	9.6 ± 0.9 a	3.8 ± 0.3 ab
Particles: 50% oil reduction	44.0 ± 1.4 b	10.2 ± 0.2 a	4.1 ± 0.1 a

*Results were expressed as means ± standard deviations, n=3. Means with different lowercase letters within the same column are significantly different ($p<0.05$).

Table 4.3. Dimensions* of puff pastries prepared from traditional shortenings or fractionated palm oil particles.

Shortening type	Diameter (D, mm)	Thickness (T, mm)	Pastry lift (T/T_0)
Butter	44.8 ± 0.1 b	14.2 ± 1.2 b	4.8 ± 0.4 b
Crisco	46.8 ± 0.4 a	8.0 ± 1.4 c	2.7 ± 0.5 c
Lard	47.0 ± 0. 8 a	7.1 ± 0.4 c	2.4 ± 0.1 c
Lard: 50% oil reduction	46.9 ± 0.5 a	7.9 ± 0.9 c	2.6 ± 0.3 c
Particles	45.3 ± 0.6 b	17.3 ± 1.4 a	5.8 ± 0.5 a
Particles: 50% oil reduction	46.0 ± 0.7 b	16.9 ± 0.7 ab	5.6 ± 0.2 a

*Results were expressed as means ± standard deviations, n=3. Means with different lowercase letters within the same column are significantly different ($p<0.05$).

Table 4.4. Dimensions* of pie crusts prepared from traditional shortenings or fractionated palm oil particles.

Shortening type	Diameter (D, mm)	Thickness (T, mm)	Pastry lift (T/T_0)
Butter	49.6 ± 1.0 a	8.1 ± 1.1 b	2.0 ± 0.3 b
Crisco	47.7 ± 0.3 a	7.9 ± 0.7 b	2.0 ± 0.2 b
Lard	50.9 ± 3.9 a	8.3 ± 0.8 b	2.1 ± 0.2 b
Lard: 50% oil reduction	46.4 ± 0.1 a	10.1 ± 1.6 b	2.5 ± 0.4 ab
Particles	48.8 ± 0.9 a	11.6 ± 1.8 a	2.9 ± 0.5 a
Particles: 50% oil reduction	49.4 ± 0.5 a	10.6 ± 1.2 ab	2.6 ± 0.3 ab

*Results were expressed as means ± standard deviations, n=3. Means with different lowercase letters within the same column are significantly different ($p<0.05$).

Table 4.5. Fracturability* of the pastries prepared from traditional shortenings or fractionated palm oil particles.

Shortening type	Biscuits (mm)	Puff pastries (mm)	Pie crusts (mm)
Butter	0.6 ± 0.1 b	10.7 ± 2.3 a	3.0 ± 1.2 bcd
Crisco	0.5 ± 0.1 b	10.5 ± 2.5 a	2.2 ± 0.9 d
Lard	1.1 ± 0.4 b	1.4 ± 0.3 b	2.6 ± 0.5 cd
Lard: 50% oil reduction	0.9 ± 0.1 b	2.7 ± 1.4 b	6.1 ± 1.5 ab
Particles	1.3 ± 0.3 ab	9.2 ± 1.2 a	5.7 ± 1.2 abc
Particles: 50% oil reduction	2.1 ± 0.6 a	9.9 ± 0.8 a	7.8 ± 1.7 a

*Results were expressed as means ± standard deviations, n=3. Means with different lowercase letters within the same column are significantly different ($p<0.05$).

Figure captions

Fig. 4.1. SEM images (a, b) and confocal fluorescence microscopy images (c, d) showing the particle morphology (adapted from Gudeman et al., 2019). (a) SEM images of the fractionated palm oil particles; (b) SEM image of the freeze-fractured fractionated palm oil particles; (c) confocal fluorescence microscopy image representing a single slice of the central location of z-scanning; and (d) was auto-adjusted with improved contrast, and represent a single slice of a deeper (after central) location of z-scanning. Blue color represents the fluorescence from Nile Red staining the background. Black color represents hollow structure in the particles; red color represents positive for Nile Red binding, indicating shell of the particles.

Fig. 4.2. Effect of shortening types and oil content on peak hardness of biscuits. FPOP: fractionated palm oil particles.

Fig. 4.3. Texture profile of the biscuits prepared using different shortenings and oil content. FPOP: fractionated palm oil particles.

Fig. 4.4. Effect of shortening types and oil content on peak hardness of puff pastries. FPOP: fractionated palm oil particles.

Fig. 4.5. Texture profile of the puff pastries prepared using different shortenings and oil content. FPOP: fractionated palm oil particles.

Fig. 4.6. Effect of shortening types and oil content on peak hardness of pie crusts. FPOP: fractionated palm oil particles.

Fig. 4.7. Texture profile of the pie crusts prepared using different shortenings and oil content. FPOP: fractionated palm oil particles.

Fig. 4.8. Effect of shortening types and oil content on biscuit appearance. FPOP: fractionated palm oil particles.

Fig. 4.9. Effect of shortening types and oil content on puff pastry appearance. FPOP: fractionated palm oil particles.

Fig. 4.10. Effect of shortening types and oil content on pie crust appearance. FPOP: fractionated palm oil particles.

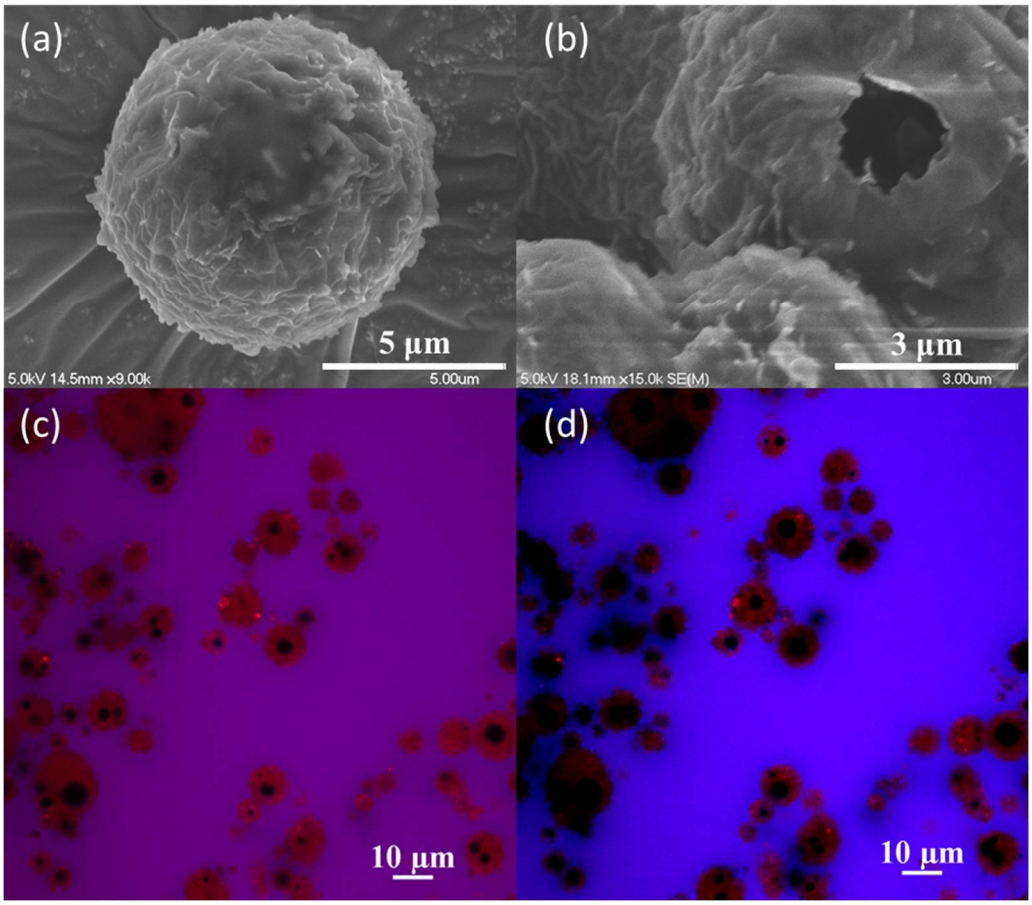
(a)
5 µm
5.0kV 14.5mm x9.00k
5.00um
(b)
3 µm
5.0kV 18.1mm x15.0k SE(M)
3.00um
(c)
10 µm
(d)
10 µm

Figure 4.1.

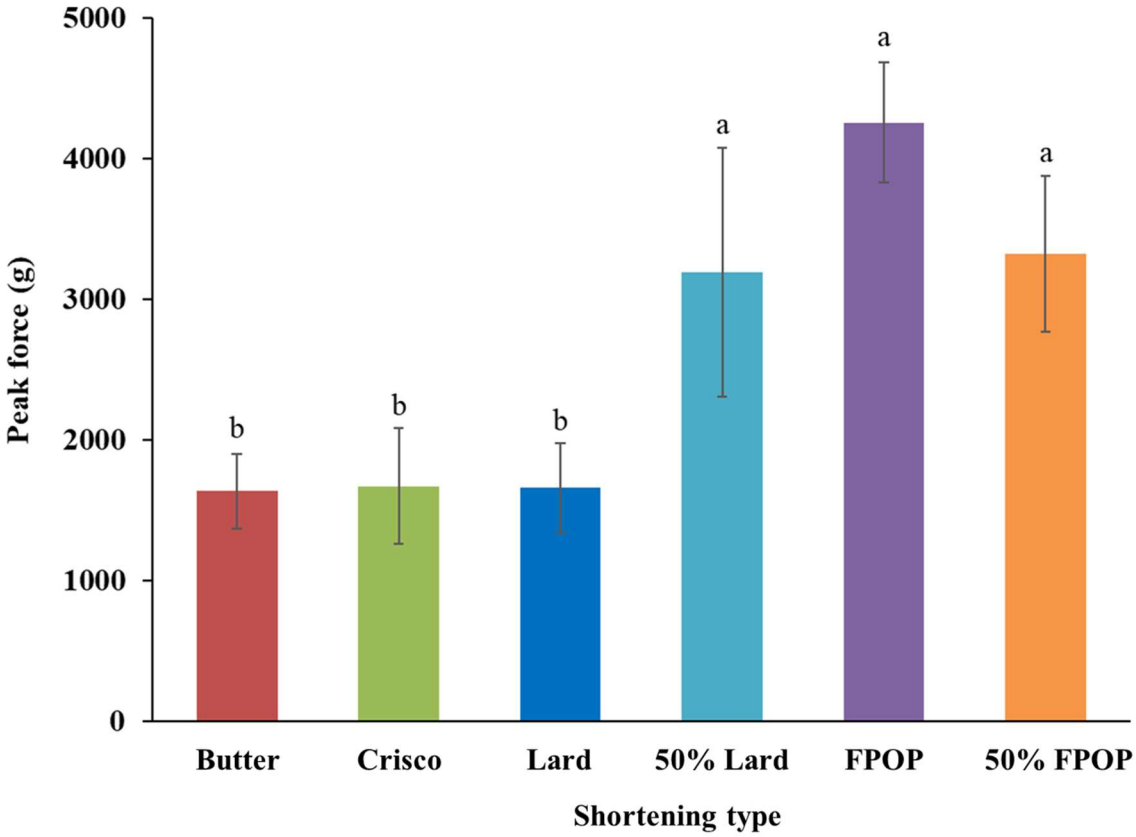
5000
4000
3000
2000
1000
0
Peak force (g)
b
b
b
a
a
a
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP
Shortening type

Figure 4.2.

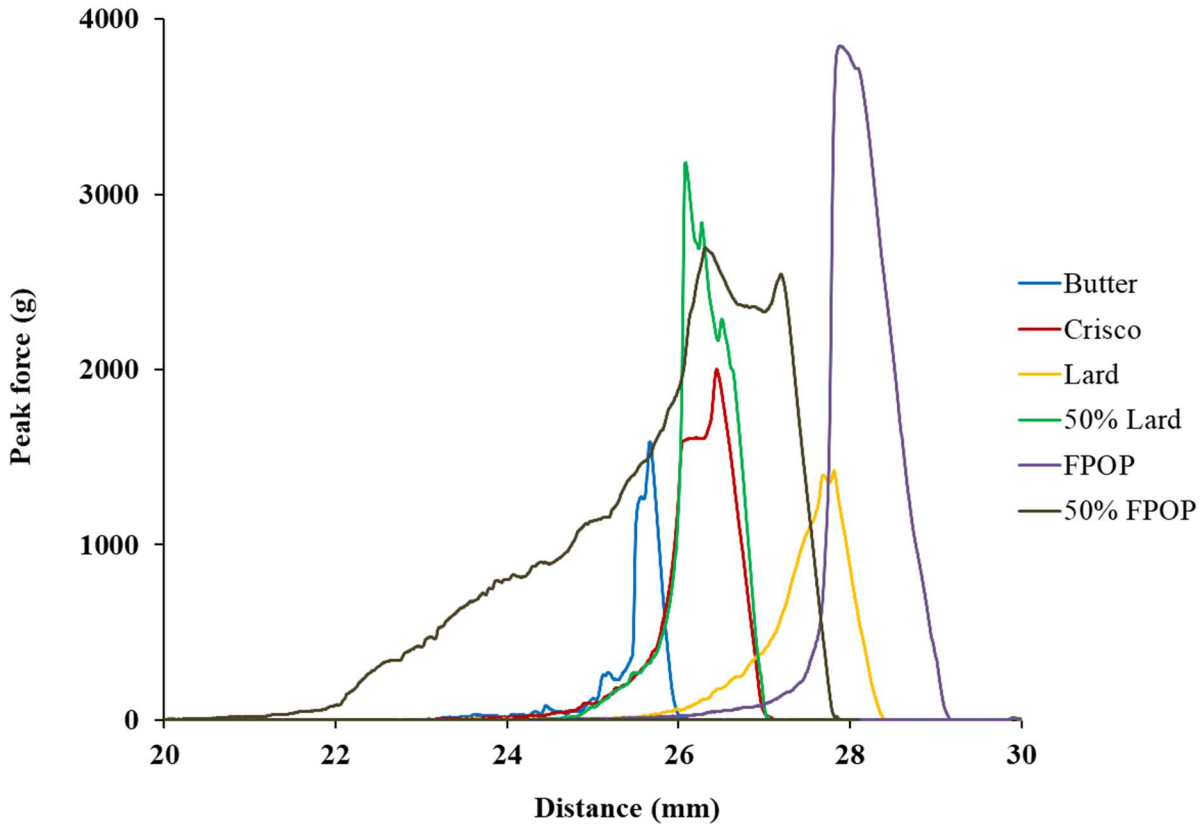
4000
3000
2000
1000
0
Peak force (g)
20
22
24
26
28
30
Distance (mm)
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP

Figure 4.3.

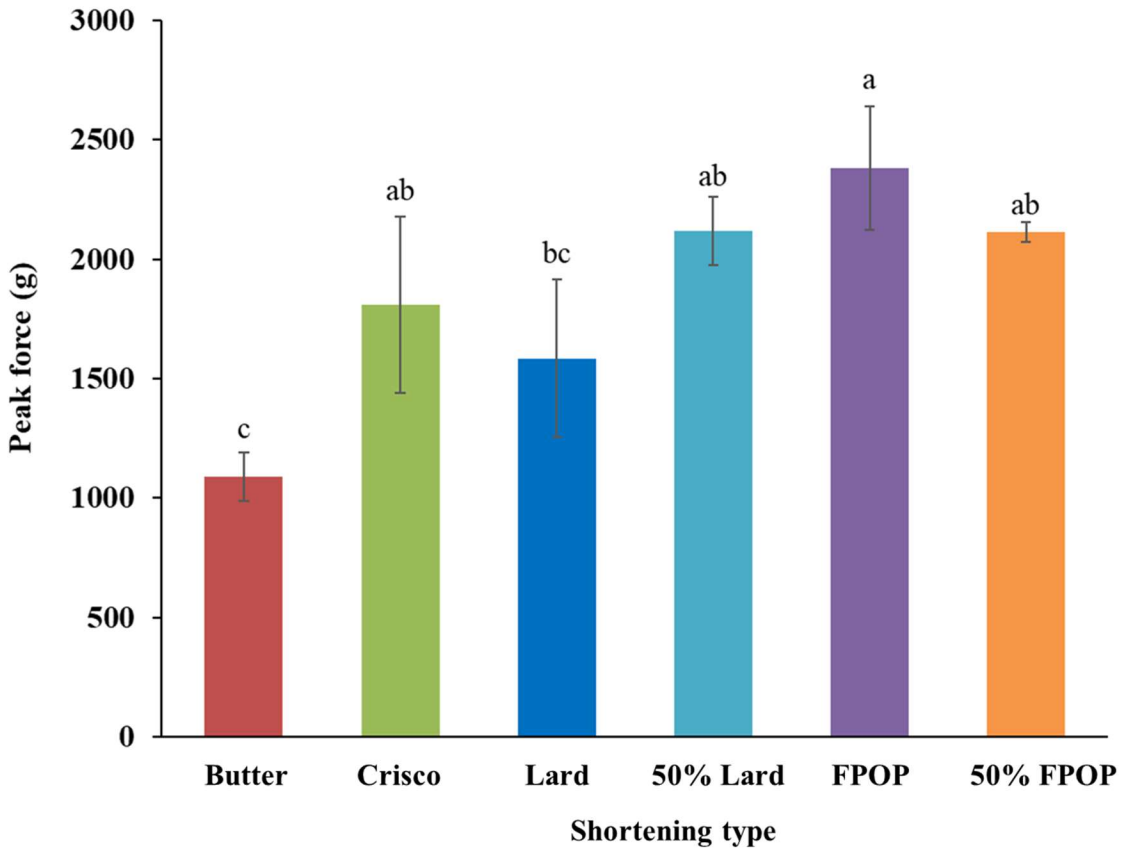
3000
2500
2000
1500
1000
500
0
Peak force (g)
c
ab
bc
ab
a
ab
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP
Shortening type

Figure 4.4.

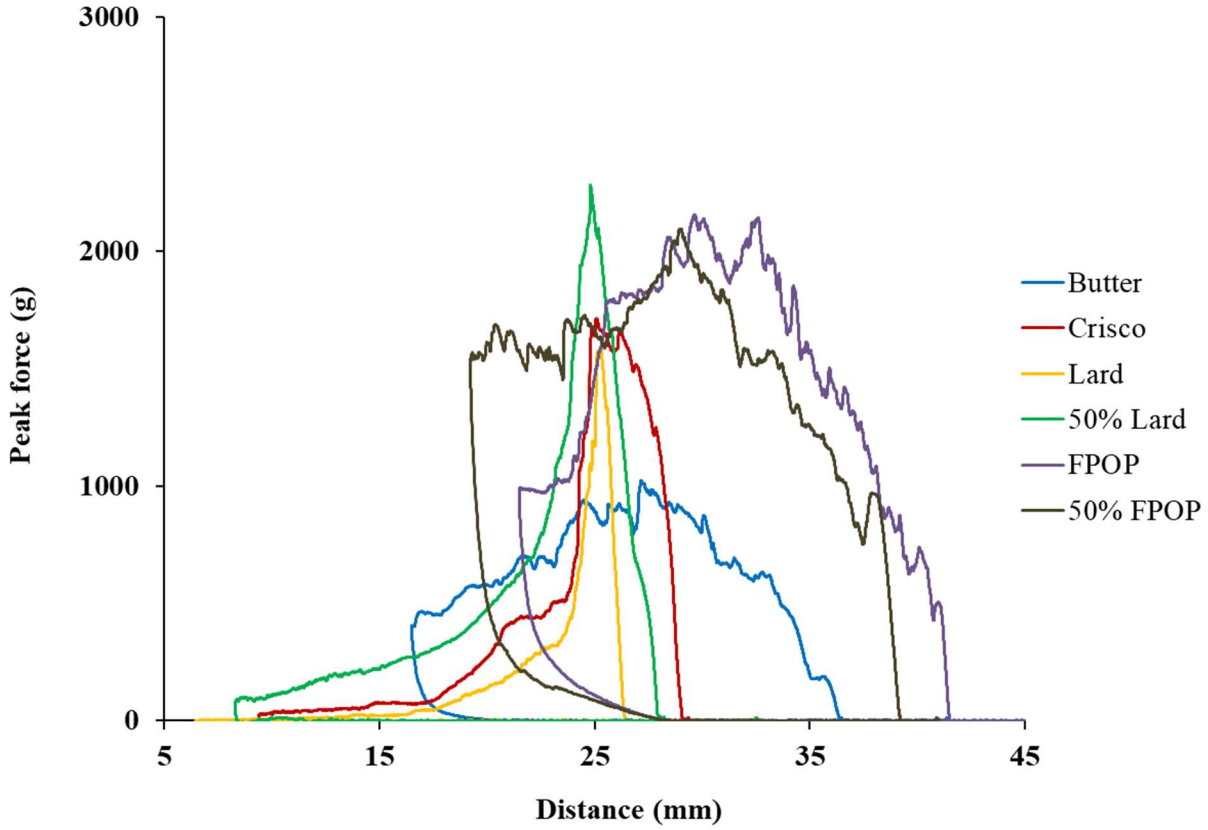
3000
2000
1000
0
Peak force (g)
5
15
25
35
45
Distance (mm)
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP

Figure 4.5.

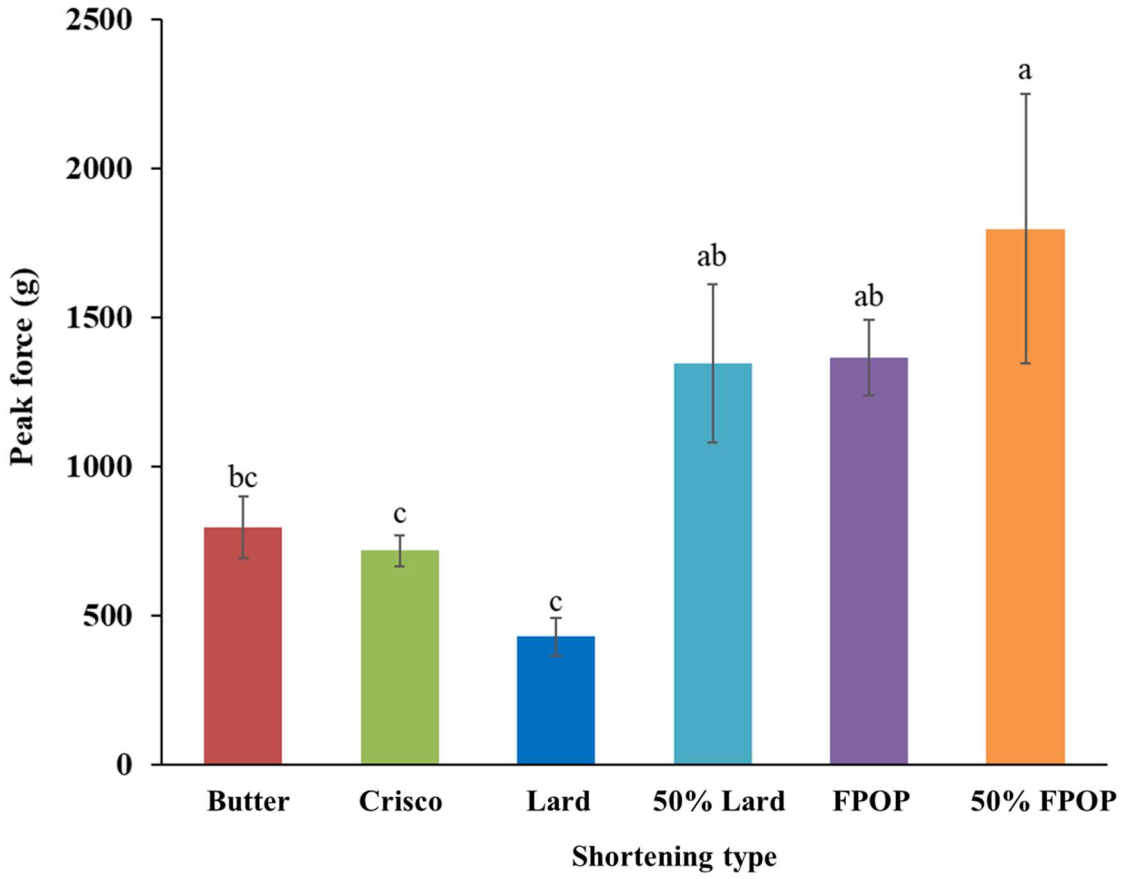
2500
2000
1500
1000
500
0
Peak force (g)
bc
c
c
ab
ab
a
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP
Shortening type

Figure 4.6.

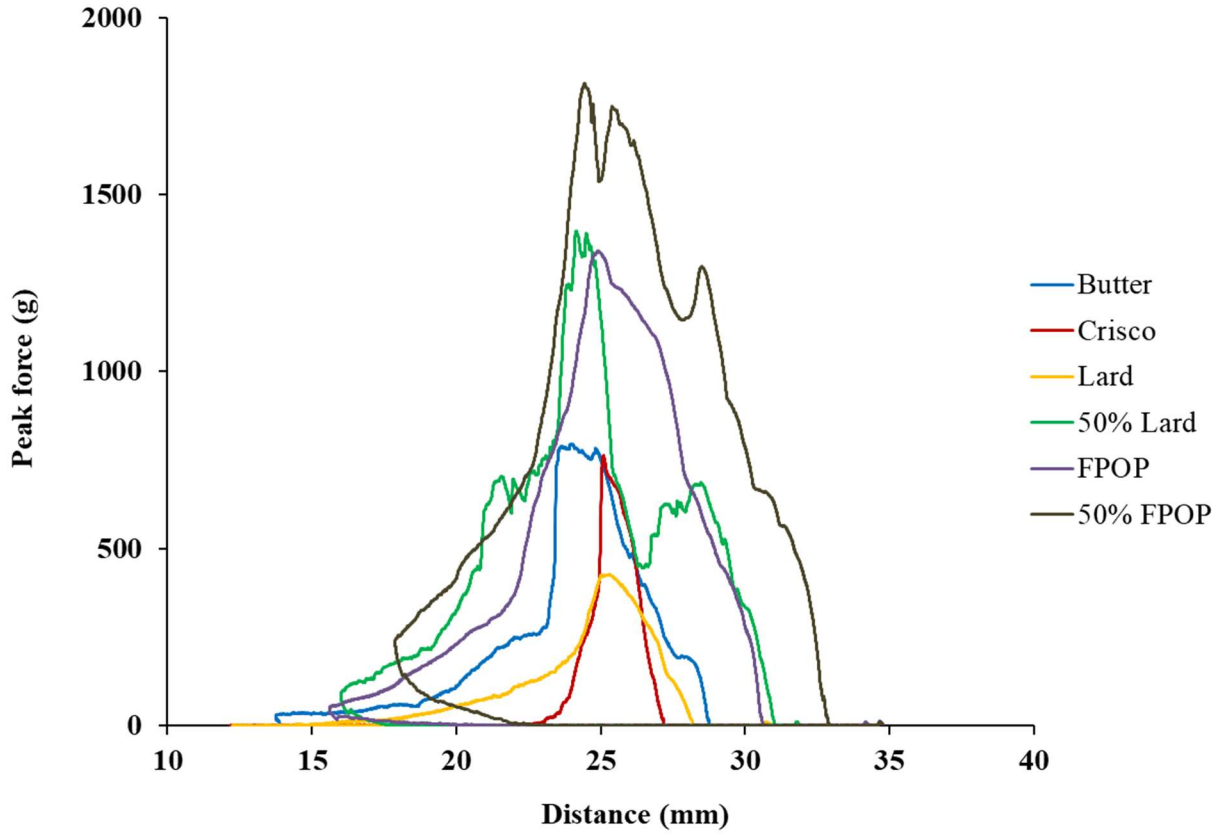
2000
1500
1000
500
0
Peak force (g)
10
15
20
25
30
35
40
Distance (mm)
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP

Figure 4.7.

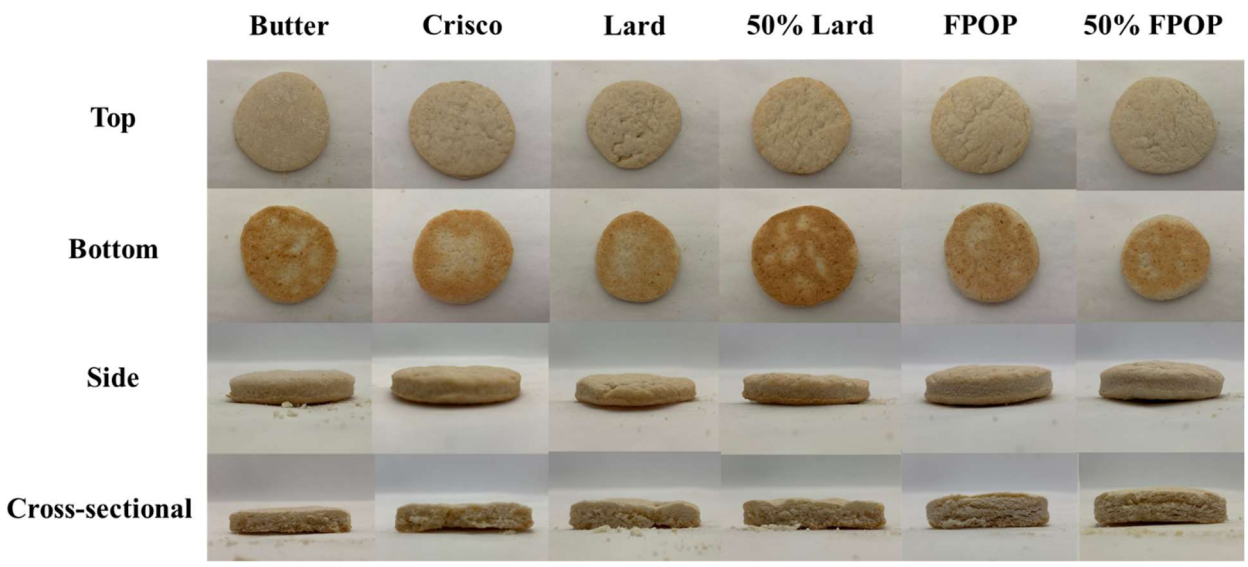
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP
Top
Bottom
Side
Cross-sectional

Figure 4.8.

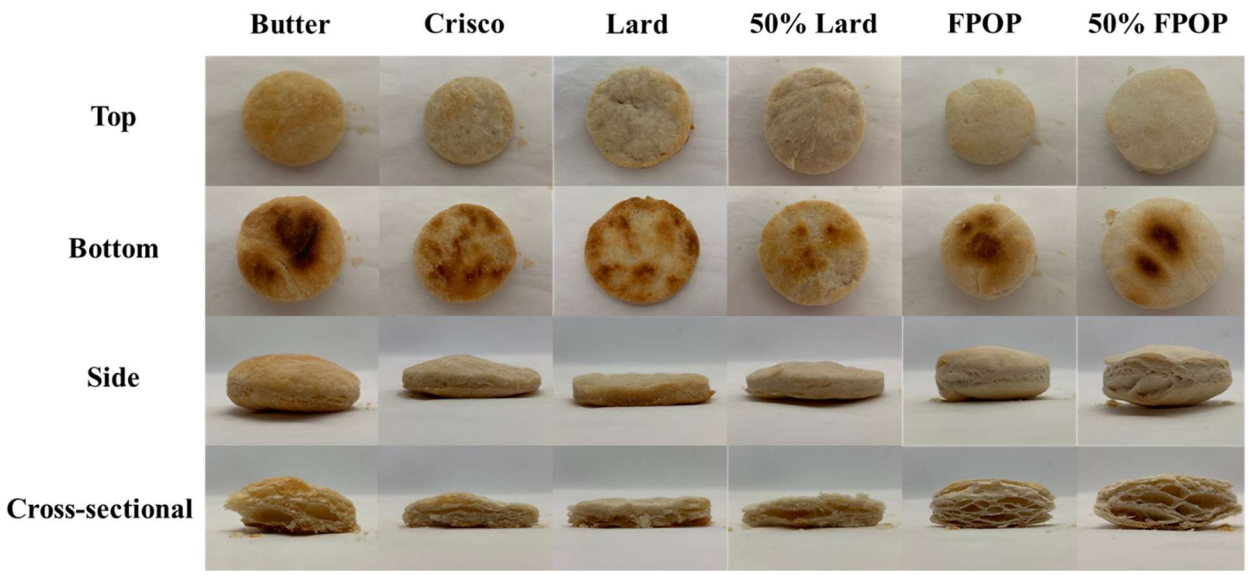
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP
Top
Bottom
Side
Cross-sectional

Figure 4.9.

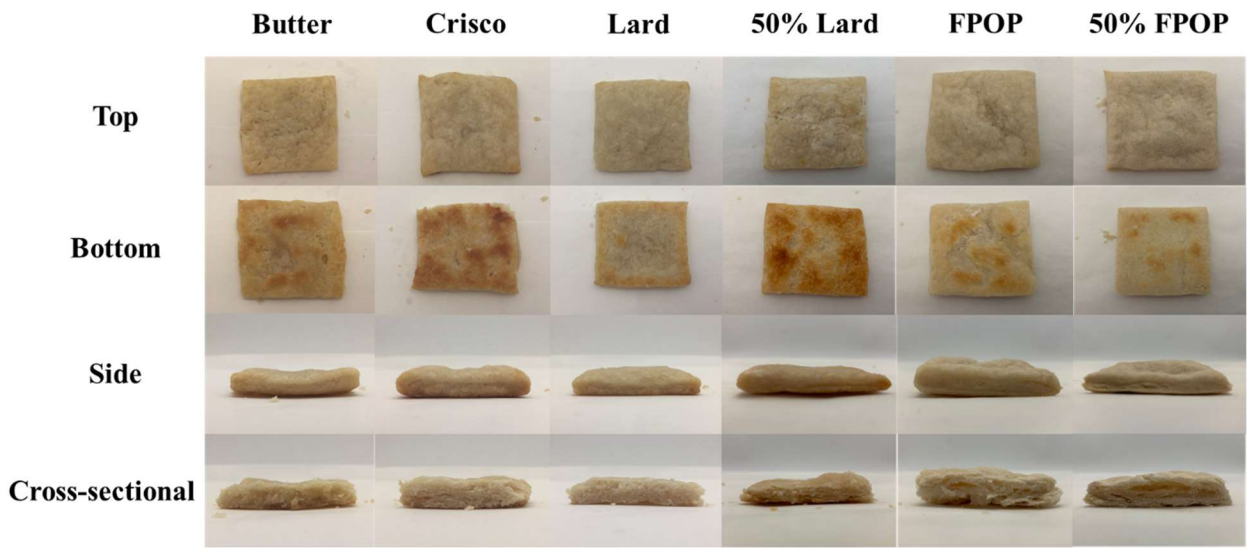
Butter
Crisco
Lard
50% Lard
FPOP
50% FPOP
Top
Bottom
Side
Cross-sectional

Figure 4.10.

CHAPTER 5. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1. Summary and conclusions

The research in this thesis has demonstrated that the atomization of supercritical carbon dioxide expanded lipids can be used to form hollow solid microparticles from non-hydrogenated oils. These microparticles were then tested in baked pastry applications where they were easier to handle and incorporate into the dough than traditional shortenings.

Chapter 3 of this thesis showed that rapid depressurization of carbon dioxide expanded, non-chemically modified lipids could be used to form hollow microparticles. Compared to the raw lipids, the microparticle formation reduced the density 5 fold, decreased melting point, and increased the surface area to mass ratio of the material. Higher melting lipid raw materials for the particle formation had more pronounced hollow structure, more spherical uniformity, and smaller particle sizes.

Chapter 4 of this thesis looked at using the lipid microparticles obtained in Chapter 3 with a baked pastry application. A key function of shortenings in pastries is to interrupt the dough gluten matrix to provide a softer, flakier texture in the finished baked good. The lipid microparticles were compared to the traditional shortenings butter, Crisco, and lard. The pastries tested were biscuits, puff pastries, and pie crusts and were chosen because the shortenings play a unique function in each pastry. Biscuits have rising with shortening distributed uniformly throughout, puff pastries have rising with shortening distributed in distinct layers, and pie crusts have no rising with shortening distributed uniformly throughout. All of the pastries made with the lipid microparticles did have firmer textures than those prepared with the traditional shortenings. The lipid microparticles being too small to properly interrupt the gluten matrix is a possible

explanation of these results. An observed benefit of the lipid microparticles was that they were easier to pour, weigh, and incorporate into the dough than the traditional shortenings that needed to be cut to size.

The lipid microparticles obtained in these studies could offer a number of potential unique benefits in food applications. Because they are free-flowing, handling, pouring, and uniformly incorporating the particles into batches could be simplified. The free-flowing nature of the particles also unlocks the potential for use of vibratory or screw feeders in continuous systems for more efficient production of formulas requiring solid fats. The high ratio of surface area to mass relative to traditional lipid formats could allow for rapid remelting when desired. The low density of these particles could also potentially provide more surface area for coating the pallet with less oil in the formula for reduced calories and material usage.

5.2. Recommendations

An interesting continuation of the pastry study in chapter 4 would be to make hollow lipid particles with a larger particle size and then repeat the pastry applications study. By changing the lipid particle production conditions like vessel pressure, vessel temperature, and nozzle diameter, larger particles could be produced. Larger lipid particles could maintain the benefits of being free-flowing, low density, incorporated uniformly into the pastry dough, and easy to handle while also potentially being large enough to properly interrupt the gluten matrix for a softer, flakier texture in the finished baked good.

Besides baked pastries, there are a number of other food applications where lipid microparticles could provide valuable benefits. Free flowing oil particles could be a convenient alternative to traditional tablespreads that require utensils and may need tempering before usage.

Oil microparticles could potentially use salt shaker like packaging for easy application onto foods, and the hollow nature of the particles would allow for quick melting if the food was warm. To better replicate the oil distribution in animal meats, vegetarian meat analogues could potentially use oil microparticles. Powdered drink mixes and creamers could use the hollow oil particles where the increased surface area to mass would allow for increased contact with the warm liquid of the drink for quick melting.

The study in chapter 3 of this thesis showed that the oils used must have a melting point well above human body temperature for formation of the particles in an ambient environment. This high melting requirement limits the types of oil that can be used to compose the particles to essentially fractionated palm oil or chemically modified (hydrogenated or interesterified) oils. Oils with melting points well above body temperature also leave an undesirable waxy mouthfeel when consumed because they do not melt on the palate. A potential solution worth exploring would be forming the lipid particles in an environment with lower temperatures. Being able to form the particles with lower melting oils would allow for the usage of a variety of oil types including palm kernel oil, coconut oil, cocoa butter, and milkfat. Decreasing the melting point of the particles below human body temperature would also provide more desirable sensory characteristics.