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Structuring Fat Foods

Suzana Caetano da Silva Lannes and
Rene Maria Ignácio

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1. Introduction

1.1. Fat roles

Food fat provides taste, consistency, and helps us feel full. Fat is a major source of energy for the body, and aids in the absorption of lipid soluble substances including vitamins A, D, E, and K. Dietary fat is essential for normal growth, development, and maintenance, and serves a number of important functions. Increasing evidence indicates that fatty acids and their derived substances may mediate critical cellular events, including activation and expression of genes, and regulation of cellular signaling [1].

When and how humans learned to use fats and oils is unknown, but it is known that primitive people in all climates used them for food, medicine, cosmetics, lighting, preservatives, lubricants, and other purposes. The use of fats as food was probably instinctive, whereas the other applications most likely resulted from observations of their properties and behavior under various environmental conditions. More than likely, the first fats used by humans were of animal origin and were separated from the tissue by heating or boiling. Recovery of oil from small seeds or nuts required the development of more advanced methods of processing, such as cooking, grinding, and pressing processes [2].

The total global oil and fat market is a huge economic factor. The rise of affluence in developing countries, this market is increasing and can be expected to increase further. The main fats commonly consumed are vegetable oils and fats, dairy fat and fats derived from animals, e.g. lard, tallow and fish oil [3].

Refining edible oils such as neutralization, bleaching, and deodorization, has been practiced for just over a century, but it has had a great impact on eating habits. Whereas the refining processes have increased the availability of sufficiently palatable oils, the oil modification

processes (hydrogenation, interesterification, and fractionation) have increased the usefulness of edible oils by increasing their interchangeability [4].

2. Fats and oils

Fats and oils are water insoluble substances that are a combination of glycerin and fatty acids called triacylglycerols. Fats appear solid at ambient temperatures and oils appear liquid. Seeds, fruits, animal, and marine sources provide oils and/or fats; however, only a few of these sources are of economic importance. Fats and oils are the most concentrated source of energy of the three basic foods (carbohydrates, proteins, and fats), and many contain fatty acids essential for health that are not manufactured by the human body. Fats and oils are commonly referred to as triacylglycerols because the glycerin molecule has three hydroxyl groups where a fatty acid can be attached. The triacylglycerol structure is affected by the present and the position of attachment (alpha, sn-1; middle, sn-2; outer, sn-3) of each fatty acid to the glycerin. The chemical and physical properties of fats and oils are largely determined by the fatty acids that they contain and their position within the triacylglycerol molecule [2].

2.1. Fatty acids

Fatty acids consist of elements, such as carbon, hydrogen, and oxygen, which are arranged as a linear carbon chain skeleton of variable length with a carboxyl group at one end. Fatty acids can be saturated (no double bond), monounsaturated (one double bond), or polyunsaturated (two or more double bonds), and are essential for energetic, metabolic, and structural activities. An unsaturated fatty acid with a double bond can have two possible configurations, either *cis* or *trans*, depending on the relative positions of the alkyl groups.

2.1.1. Fatty acids occurrence

The fatty-acid carbon-chain lengths vary between 4 and 24 carbon atoms with up to three double bonds, with C18 the most common. Over 1000 fatty acids are known with different chain lengths, positions, configurations and types of unsaturation, and a range of additional substituents along the aliphatic chain. However, only around 20 fatty acids occur widely in nature; of these, palmitic, oleic, and linoleic acids make up ~80% of commodity oils and fats[4].

The most prevalent saturated fatty acids are lauric (C-12:0), myristic (C-14:0), palmitic (C-16:0), stearic (C-18:0), arachidic (C-20:0), behenic (C-22:0), and lignoceric (C-24:0). The most important monounsaturated fatty acids are oleic (C-18:1) and erucic (C-22:1). The essential polyunsaturated fatty acids are linoleic (C-18:2) and linolenic (C-18:3) [2].

2.1.2. Saturated fatty acids

Saturated fatty acids contain only single carbon-to-carbon bonds and are the least reactive chemically [2]. Saturated acids with 10 or more carbons are solids, and melting points increase with chain length. Melting points alternate between odd and even chain length, with odd chain

lengths having a lower melting point than the preceding even chain acid [4]. Most of the saturated fatty acids occurring in nature have unbranched structures with an even number of carbon atoms. These acids range from short-chain-length volatile liquids to waxy solids having chain lengths of ten or more carbon atoms. Fatty acids from 2 to 30 carbons (or longer) do occur, but the most common and important acids contain between 12 and 22 carbons and are found in many different plant and animal fats. Saturated fatty acids are also functionally divided into short- and long-chain acids and are most widely known by their trivial names. The short-chain saturated acids (4:0–10:0) are known to occur in milk fats and in a few seed fats [1]. Medium chain fatty acids (8:0, 10:0, 12:0, and 14:0) occur together in coconut and palm kernel oils, both tropical commodity oils. In both of these oils, lauric acid (12:0) predominates (45 to 55%). Palmitic acid (16:0) is the most abundant and widespread natural saturated acid, present in plants, animals, and microorganisms. Palm oil is a rich commodity oil source and contains over 40% of palmitic acid. Stearic acid (18:0) is also ubiquitous, usually at low levels, but is abundant in cocoa butter (~34%) and some animal fats, e.g., lard (5 to 24%) and beef tallow (6 to 40%). A few tropical plant species contain around 50 to 60% of 18:0 [4]. The long-chain saturated acids (19:0 and greater) are major components in only a few uncommon seed oils.

2.1.3. *Unsaturated fatty acids*

Unsaturated fatty acids contain one or more carbon-to-carbon double bonds and are liquid at room temperature with substantially lower melting points than their saturated fatty acid counterparts. Monounsaturated fatty acids have only one double bond in the carbon chain and polyunsaturated fatty acids have two or more double bonds in the carbon chain [2]. Polyunsaturated fatty acids, sometimes referred to as PUFAs or polyalkenoic acids, can be divided into conjugated (double-bonded carbon atoms alternate with single bonds) and unconjugated (double bonds are separated by one or more carbon atoms with only single bonds) [1].

The most common monounsaturated is oleic acid (18:1 9c). Oleic acid is found in most plant and animal lipids and is the major fatty acid in olive oil (70 to 75%) and several nut oils, e.g., macadamia, pistachio, pecan, almond, and hazelnut (filbert) contain 50 to over 70%. High oleic varieties of sunflower and safflower contain 75 to 80% oleic acid. *Cis*-monounsaturated with 18 or less carbons are liquids at room temperature or low-melting solids; higher homologues are low-melting solids. *Trans*-monounsaturated are higher melting, closer to the corresponding saturated acids. Double bond position also influences the melting point; both *cis*- and *trans*-C18 monounsaturated are higher melting when the double bond is at even positions than at odd positions [4]. Saturated fatty acids are very stable, but unsaturated acids are susceptible to oxidation; the more double bonds the greater the susceptibility. Unsaturated fatty acids, therefore, have to be handled under an atmosphere of inert gas (e.g. nitrogen) and kept away from oxidants or substances giving rise to free radicals [5].

2.1.4. *Trans fatty acids*

Monosaturated and methylene-interrupted polyunsaturated fatty acids are predominantly *cis*. *Trans* isomers, mainly monosaturated, are produced during catalytic partial hydrogenation,

and can be present in substantial amounts in hardened fats, generally as a mixture of positional isomers. Heat treatment during deodorization of commodity oils may result in low levels of *trans* isomers, particularly of polyunsaturated. The undesirable nutritional properties of *trans* fatty acids have led to alternative ways of producing hardened fats, such as interesterification or blending with fully saturated fats, and to the use of milder deodorization procedures [4]. It is important to note that *trans* double bonds do occur in natural fats, as well as in industrially processed fats, but generally much less abundantly than *cis* bonds. Thus some seed oils have a significant content of fatty acids with *trans* unsaturation [5]. Saturated and *trans* fatty acids have a higher melting point than unsaturated and *cis* fatty acids [1].

2.1.5. Health problems

Concerns about possible toxic effects of fatty acids with *trans*-unsaturation began with the publication of results of experiments with pigs given diets containing hydrogenated vegetable fat for 8 months. They had more extensive arterial disease than those given otherwise equivalent diets devoid of *trans*-unsaturated fatty acids. Subsequently, numerous animal feeding trials, epidemiological studies of human populations and controlled dietary experiments with human subjects have been reported [5]. In January 2003 the US Food and Drug Administration (FDA) instituted a requirement to list *trans* fat content as a separate item on the Nutrition Facts label on packaged foods from 2006. This change in labeling requirements has served as a catalyst to accelerate food product reformulation. On a voluntary basis, many food manufacturers and restaurants have reformulated their products and modified their operations to reduce *trans* fats in their offerings [6, 7].

Consumption of *trans* fatty acids raise the level of low density lipoprotein (LDL) cholesterol and decrease the level of high density lipoprotein (HDL) cholesterol. Based on results of epidemiological and intervention studies it is clear that these changes in blood profiles increase the risk of coronary heart diseases. The main food sources for *trans* fatty acids are cookies and confectionary, snacks, and frying fats [8]. Consumption of significant amounts of *trans* fatty acids has been a major health concern for consumers and regulatory agencies over the past decade. The major dietary sources of *trans* fatty acids are products formulated with partially hydrogenated fats. Examples include margarines, shortenings, bakery products, and fast foods. The regulatory mandate from FDA and consumer concerns have led to the development of alternative processes to produce foods with zero or reduced *trans* fatty acids contents [7, 9].

Fats and oils can be formulated as *trans*-acid-free products, but saturates are required for the solids contents that provide the functionality for plastic and liquid products. Reduced saturates may be an option in some cases, but a saturate-free product is probably impossible if functionality is to be maintained [2]. Obviously, if the fat is completely hydrogenated there will be no double bonds and hence no problem; however, partially hydrogenated fats have *trans* double bonds. *Trans* double bonds are rare in naturally occurring fats, the major natural source is milk fat because they are formed by bacterial action in the rumen. So, most naturally occurring oils and fats have *cis* double bonds; however, some *trans* double bonds are found in milk fat and some marine oils.

2.1.6. Low-trans

The new rules about *trans* fatty acids promise to strongly affect what is acceptable to consumers and food manufacturers. It will be difficult to meet all the demands for low-*trans* fats and other traits that are important to consumers with the current technology, especially for frying fats and oils. Seed suppliers are busy trying to furnish seeds with compositions that will meet these needs and find farmers to grow these crops. Contracts with oilseed processors have been made to process the harvest. Some food companies have pledged to use only *trans*-free fats and oils in their products [1].

Trans-free fat blends can be constructed by blending oils with fully hardened oils, or indeed where the entire blend has been randomized through interesterification. Blending vegetable oil types from different sources is an efficient alternative to hydrogenated vegetable oils, and still provides the appropriate physicochemical properties and nutritional requirements demanded. Such fat blends can also be rich in polyunsaturated fatty acids as well as being *trans*-free. *Trans*-free options are commercially available in the form of a blend of tailored emulsifiers and oil blends where they meet demands for shelf-life, processing and distribution requirements. These *trans*-free options are available for a wide range of products covering, snacks, cakes, breads, tortillas, nutrition bars, cookies and breakfast cereals. *Trans*-free oil blends are also routinely designed for margarines, where they impart structure and texture, and shortenings where they provide firmness and contribute to crumb structure [10]. The combination of *trans*-free modification techniques (full hydrogenation, interesterification and fractionation) and the availability of a variety of different feedstocks can be used to produce virtually *trans*-free hardstocks with a range of physical properties such as solid phase lines determining melting performances. Liquid seed oils, low in solids, are first fully hydrogenated to generate solids combined with a very low *trans* level (<1.25%). These fully hydrogenated oils may subsequently be interesterified with non-hydrogenated liquid oil to reduce the solid fat content at high temperature (>40°C). This solid fat content can be further reduced by fractionation [11].

2.2. Structural characteristics

Fats are the main structural components in many food products such as chocolate, confectionery coatings, dairy products, butter, cream shortenings, margarine, and spreads. The sensory characteristics of fat-structured materials such as spreadability, hardness, and mouth feel are highly dependent on the structure of the underlying fat crystal network. This fat crystal network is built by the interaction of polycrystalline fat particles. The amount, geometry, and spatial distribution of solid fat crystals as well as their interactions at different levels within the network all affect the rheological properties of fats and fat-structured food products. Fat crystallization largely determines consistency, physical stability, visual appearance, and eating properties [4, 12, 13].

2.2.1. Crystals

A crystal consists of a material in a solid state in which the building entities—molecules, atoms or ions—are closely packed so that the free energy of the material is at minimum. As

a result the entities are arranged in a regularly repeating pattern or lattice and are affected by the following points [14]: the molecules, or atoms, or ions are subject to heat motion; only the average positions will be fixed; diffusion can occur in a crystalline material, but the time scales involved are centuries rather than seconds; incorporation of a foreign molecule leading to a dislocation in the crystal lattice (Figure 1b); some solid materials are “polycrystalline”, i.e., they are composites of many small crystalline domains of various orientations (Figure 1c).

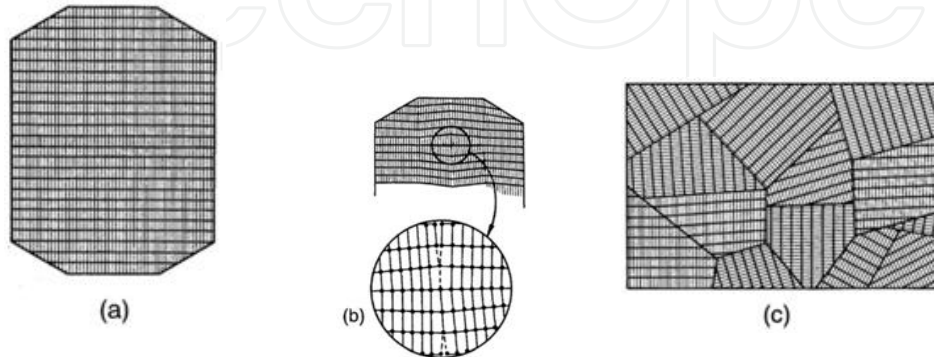


Figure 1. Two-dimensional illustration of crystalline order: (a) crystal lattice with perfect order, (b) a defect in the crystal leading to a dislocation in the lattice, (c) a polycrystalline material [14].

Different lattice arrangements and unit cells (Figure 2) can be constructed in terms of the lattice parameters, also known as Bravais lattices: three spatial dimensions - a , b , and c ; and three angles - α , β , and γ . For example, cubic systems all must have equal lengths ($a=b=c$) and angles equal to 90° [15].

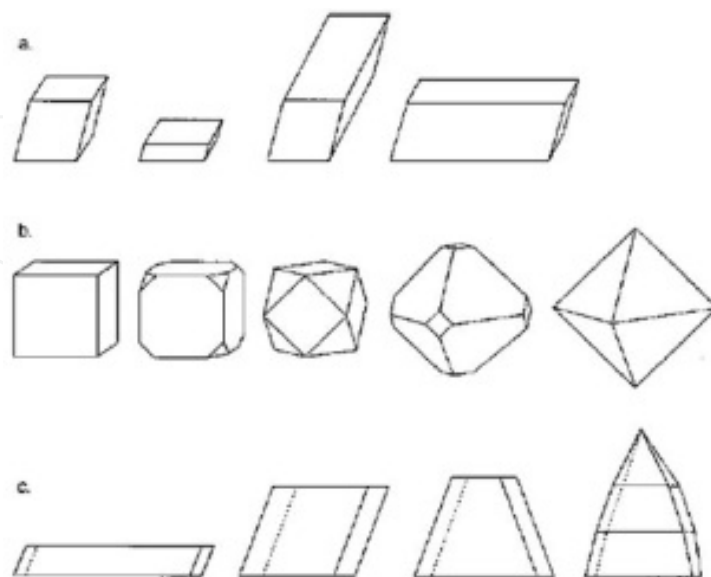


Figure 2. Variation in crystal morphology for identical unit cells: (a) rhombohedral, (b) cubic, and (c) monoclinic [15].

Crystals show enormous variation in external shape or habit caused by variation in the growth rate of the various faces of a crystal, which rates often depend on the composition of the solution. Corners and edges are rounded; curved faces can appear in large crystals; some needlelike crystals have a slight twist; some faces can grow faster than others (Figure 4). A noncrystalline solid is often referred to as an amorphous solid. Whether a material is crystalline or not can be established by x-ray diffraction. X-rays have a very small wavelength, of the order of 0.1 nm, which implies that individual atoms may cause scattering. If the atoms (or small molecules) occur at regular distances, sharp diffraction maxima occur, and the crystal structure can be derived from the diffraction pattern [14].

2.2.2. Crystallization

Many of the sensory attributes such as spreadability, mouthfeel, snap of chocolate, texture, etc., are dependent on the mechanical strength of the underlying fat crystal network. In addition to this obvious industrial importance, fat crystal networks form a particular class of soft materials, which demonstrate a yield stress and viscoelastic properties, rendering these plastic materials. The levels of structure in a typical fat network are defined as the fat crystallizes from the melt. The growth of a fat crystal network can be visualized thus: the triacylglycerols present in the sample crystallize from the melt into particular polymorphic/polytypic states. These crystals grow into larger microstructural elements ($\approx 6 \mu\text{m}$) which then aggregate via a mass- and heat-transfer limited process into larger microstructures ($\approx 100 \mu\text{m}$). The aggregation process continues until a continuous three-dimensional network is formed by the collection of microstructures. Trapped within this solid network structure is the liquid phase of the fat [12].

The crystallization process consists of two steps: nucleation and crystal growth. Nucleation can be described as a process in which molecules come into contact, orient and interact to form highly ordered structures, called nuclei. Crystal growth is the enlargement of these nuclei. Nucleation and crystal growth are not mutually exclusive: nucleation may take place while crystals grow on existing nuclei [16].

Nucleation can only be achieved via supersaturation or supercooling. A solution is supersaturated if it contains more of a component than can be theoretically dissolved within it at a particular temperature. Supercooling refers to the degree to which the solution is cooled with respect to the melting temperature of the crystallized solution. It is very difficult to determine the parameters of supersaturation and supercooling for a crystallizing system, and therefore, as a good approximation, in practice only supercooling is usually considered for crystallization of triacylglycerol molecules from the melt [17].

When the temperature of a fat melt is decreased below its maximum melting temperature, it becomes supersaturated in the higher-melting triacylglycerol species present in the mixture. This so-called undercooling or supercooling represents the thermodynamic driving force for the change in state from liquid to solid. Fats usually have to be undercooled by at least 5-10°C before they begin to crystallize. For a few degrees below the melting point, the melt exists in a so-called metastable region. In this region, molecules begin to aggregate into tiny clusters called embryos. At these low degrees of undercooling, embryos continuously form

and breakdown, but do not persist to form stable nuclei. The energy of interaction between triacylglycerol molecules has to be greater than the kinetic energy of the molecules in the melt so as to overcome Brownian effects. For these flexible molecules, it is not sufficient to simply interact; molecules have to adopt a specific conformation in order to form a stable nucleus. The adoption of this more stable conformation is relatively slow, thus explaining the existence of a metastable region. As the undercooling is increased (i.e., at lower temperatures) stable nuclei of a specific critical size are formed [18].

2.2.3. Polymorphism

An important way to characterize fats and oils is through the predominant crystalline phase, or polymorph, that tend to form upon crystallization. When the same ensemble of molecules can pack in different arrangements on crystallization, depending on the processing conditions, the substance is said to demonstrate polymorphism. The different polymorphic states of a particular substance often demonstrate quite different physical properties (such as melting behavior and hardness), but on melting yield identical liquids [17].

Polymorphism is the ability of long-chain compounds such as fatty acids to exist in more than one crystal form, and this results from different patterns of molecular packing in the crystals. Triacylglycerols may occur in three main forms, namely, α , β' , and β in order of increasing stability and melting point. When fats are cooled, crystals of a lower melting form may be produced. These may change slowly or rapidly into a more stable form. The change is monotropic, that is, it always proceeds from lower to higher stability. Polymorphism results in the phenomenon of multiple melting points. When a fat is crystallized in an unstable form and heated to a temperature slightly above its melting point, it may resolidify into a more stable form [1]. The polymorphs differ in stability, melting point, melting enthalpy, and density. The α -polymorph is the least stable and has the lowest melting point, melting enthalpy, and density. The β -polymorph is the most stable and has the highest melting point, melting enthalpy, and density. The β' -polymorph has intermediate properties [4].

Under rapid cooling conditions, triacylglycerol molecules usually crystallize in metastable polymorphic forms, which subsequently transform into polymorphs of higher stability. On the other hand, at slow cooling rates, triacylglycerol molecules of similar chain lengths have time to associate with each other in more stable geometrical arrangements, resulting in the formation of a more stable polymorphic form. Due to the dependence of fat crystallization on the degree of undercooling and the cooling rate used, different results will be observed when using different cooling rates [18].

2.2.4. Tempering

Before its solid fat content can be determined, the fat must be exposed to a prescribed temperature profile: first it has to be melted completely to destroy all traces of crystals, and then cooled to achieve virtually complete crystallization, and finally it has to be held at the measuring temperature to come to equilibrium at that temperature. Sometimes, depending on the fat used, an extra step is introduced where the fat is held at a particular temperature, which

is not the measuring temperature. This step is referred to as a tempering step. For confectionery fats, a tempering step of 40 hours at 26°C is mentioned in the standard methods to ensure that cocoa butter and similar fats like cocoa butter equivalents (CBEs) are converted to their β -polymorph before the SFC is measured [4].

Tempering is a technique of controlled pre-crystallization employed to induce the most stable solid form of cocoa butter, a polymorphic fat in finished chocolates. The process consists of shearing chocolate mass at controlled temperatures to promote crystallization of triacylglycerols in cocoa butter to effect good setting characteristics, foam stability, demoulding properties, product snap, contraction, gloss and shelf-life characteristics. Time–temperature protocols and shearing are employed to induce nucleation of stable polymorphs with the formation of three-dimensional crystal network structure influencing the microstructure, mechanical properties and appearance of products. The crystal network organization and the polymorphic state of the triacylglycerols crystals as affected by the crystallization conditions are major factors determining rheological and textural properties of crystallized triacylglycerols systems [19].

2.2.5. *Solid fat content*

The solid fat content (SFC) is a measure of the percentage of solid, crystalline fat in a sample at a selected temperature. Often, the SFC is measured at selected points within a temperature range. A measure of the SFC can be determined by a variety of methods: dilatometry, pulsed nuclear magnetic resonance (p-NMR), or differential scanning calorimetry (DSC). The method used and differences in the way it is executed can seriously affect the final result [4].

2.3. Fat design

Each application area requires its proper fat. The specifications of the fat depend on: recipe, equipment, procedure, temperature of fat and other ingredients, ambient temperature, storage and distribution temperature of the final product. Some conditions to attend a satisfactory fat design must be the compatibility among the components of the mixture: equivalent thermal properties (solid fat content, melting point and range); similar molecular size, shape and packing (to allow isomorphous replacement or formation of a single lattice unit in mixtures); similar polymorphism (transformation from stable to unstable forms should occur as readily for binary mixtures as with individual components) (Figure 3).

2.3.1. *Processing*

Edible fats and oils have been separated from animal tissues, oilseeds, and oil-bearing fruits for thousands of years. The combined largest source of vegetable oils is the seeds of annual plants grown in relatively temperate climates. The oilseeds are processed by expeller or screw press extraction, by prepress solvent extraction, or bay expander–solvent extraction. A second source of vegetable oil is the oil-bearing tree fruits and kernels. Oil-bearing fruits are pressed to obtain oil, sometimes after drying or sterilizing, or are cold pressed to preserve flavor and odor. Animal tissues may be wet- or dry-rendered (cooking processes) to sepa-

rate the fats. Edible meat fats are supplied by lard from pigs, tallow from cattle and sheep, and milk fat or butter from cows. After recovering, fats and oils can be physically and/or chemically refined. Chemical refining removes most impurities with an alkaline solution, whereas physical refining removes them by distillation [2].



Figure 3. Physical and chemical functions of fats.

2.3.1.1. Industrialization

Searching for fat substitutes started in France during the Industrial Revolution. Large population shifts from farms to factories and, in France, a depression and an imminent war with Prussia, created a demand for butter that the milk supply could not meet, escalating butter prices. The first acceptable butter substitute, named “margarine”, was produced by the French chemist Mege Mouriés in 1869, on commission from Emperor Napoleon. Soon after the introduction of the first butter substitute on the market, several inventors patented various modifications of Mouriés’ process [2, 4, 17]. Before 1900, animal fats were used as sources of fat with a high content of solids in margarine production. This led to a shortage of animal fats since they were also the main feedstock for soap making [3]. The best known modification processes applied today in the edible oil industry are hydrogenation, interesterification (chemical or enzymatic) and fractionation. The main purpose of these processes is to change the physicochemical properties of the oil or fat, by reducing the degree of unsaturation of the acyl groups (hydrogenation), by redistributing the fatty acids chains (interesterification) or by a physical separation of the triacylglycerols through selective crystallization and filtration (fractionation) [20].

2.3.1.2. Hydrogenation

Based on work done by the French chemist Paul Sabatier on the metal-catalyzed hydrogenation of unsaturated organic compounds, German chemist Wilhelm Normann developed the method for hydrogenation of edible oils in 1903. Chemically, the hydrogenation of oils is the reduction of the double bonds in unsaturated fatty acids to single saturated bonds, by the reaction of hydrogen gas in the presence of a metal catalyst. The metal catalyst used at the

time was nickel, and it has practically remained the same in the current hydrogenation procedures. Complete reduction of all double bonds in the oil would yield 100% saturated fatty acids, whereas reduction of only a fraction of the double bonds results in partially hydrogenated fats. During the process of hydrogenation the *cis* double bond can open up and reform into a *trans* double bond, as well as shift positions along the fatty acid carbon chain. Structurally, *cis* double bonds in unsaturated fatty acids produce a bend in the chain that prevents unsaturated fatty acids from packing as tightly as saturated fatty acids. As a consequence, a *cis* unsaturated fatty acid has a lower melting point than a saturated fatty acid with the same molecular weight. Conversely, the *trans* double bonds do not create a bend on the fatty acid chain. Therefore, *trans* unsaturated fatty acid chains are virtually straight, resembling saturated fatty acids, and display higher melting points than the corresponding *cis* isomers [21].

The aim of the hydrogenation process is the total or partial saturation of the double bonds of unsaturated fats to obtain hard or plastic fats or to improve the stability to oxidation of an oil. The obtained product depends on the nature of the starting oil, the type and concentration of the catalyst used, the concentration of hydrogen, and the experimental conditions under which the reaction takes place. Nickel catalyst was reported to catalyze undesirable side reactions such as *cis*, *trans* isomerization and positional isomerization of double bonds. The position of the double bonds affects the melting point of the fatty acid to a limited extent. The presence of different geometric isomers of fatty acids influences the physical characteristics of the fat to a greater extent [22].

2.3.1.3. *Interesterification*

Interesterification has been developed as an alternative to hydrogenation, with the specific aim of eliminating the formation of *trans* fatty acids. The process rearranges the distribution of the fatty acids either chemically or enzymatically, within and between the triacylglycerols, thus the fatty acid distribution is altered, but the fatty acid composition remains unchanged – this rearrangement can be done either in a random or controlled manner. The technique is effective and can be used to produce fat products for spreads that are soft and spreadable and also *trans*-free. Interesterification is nothing new, having been around for some time, and the basic principles were first documented in 1969 [10].

2.3.1.4. *Fractionation*

Fractionation is a fully reversible modification process; it is basically a thermo-mechanical separation process in which a multi-component mixture is physically separated into two or more fractions with distinct physical and chemical properties. The separation can be based on differences in solidification, solubility, or volatility of the different compounds: fractional crystallization, fractional distillation, short-path distillation, supercritical extraction, liquid-liquid extraction, adsorption, complexation, membrane separation, etc. are the main techniques practiced. Fractional crystallization refers to a separation process in which the fatty material is crystallized, after which the liquid phase is separated from the solid. It is based on differences in solubility of the solid triacylglycerol in the liquid phase, depending on

their molecular weight and degree of unsaturation; this is a consequence of the ability of fats to produce crystals. On an industrial scale, crystals can be obtained according to three main technologies: detergent fractionation, solvent fractionation and dry fractionation [20].

2.3.2. Fat replacers

Fat replacers are called by many synonyms with various nuances in their usage: fat *replacers* can provide some or all of the functions of fat; fat *substitutes* resemble conventional fats and oils and provide all food functions of fat; fat *analogs* provide food with many of the characteristics of fat; fat *extenders* optimize the functionality of fat; fat *mimetics* mimic one or more of the sensory and physical functions of fat in the food.

Fat replacers are most frequently used to replace fat in products with a high fat content and are used in a variety of food products, including frozen desserts, processed meats, cheese, sour cream, salad dressings, snack chips and baked goods. At the height of the interest in low-fat foods, more than 1000 fat-modified foods were introduced, with fat modified snacks being the fastest growing category of products in supermarkets at the time [11]. Normal fat contains nine calories per gram compared with five calories per gram for the sugar and protein components. If the proportion of fat is reduced the calorific value will fall. Corn starch, maltodextrin, pectin, gelatin, xanthan gum, guar gum, carrageenan, and soy protein were all commonly used ingredients in reduced fat products launched in the period 2008–10. Low in saturated fatty acids, sunflower oil was commonly used in new reduced fat foods. Fat replacers of the future will need to meet some important criteria, including reducing or replacing the target fat effectively, being available at a cost appropriate to the benefits provided, and being safe and legal with no appreciable side effects.

2.3.3. Shortening

Shortening was the term used to describe the function performed by naturally occurring solid fats such as lard and butter in baked products. These fats contributed a “short” (or tenderizing) quality to baked products by preventing the cohesion of the flour gluten during mixing and baking. Shortening later became the term used by all-vegetable oil processors when they abandoned the lard-substitute concept. Shortening has become virtually synonymous with fat and includes many other types of edible fats designed for purposes other than baking. Currently, a description for shortening would be processed fats and oils products that affect the stability, flavor, storage quality, eating characteristics, and eye appeal of prepared foods by providing emulsification, lubricity, structure, aeration, a moisture barrier, a flavor medium, or heat transfer [2].

Fats and oils added to breads, cakes and similar baked goods are often referred to as shortenings that contribute to tenderness, improve volume gain of bread dough, enhance texture, crumb structure and shelf-life of the products. In order to produce a satisfactory shortening, one has to pay specific attention to the crystal structure, and similarly the consistency of the shortening will depend on the ratio of solid to liquid fat present at different temperatures [10].

Plastic shortening describes fats that are readily spread, mixed or worked. The property of plasticity is highly important in fats used as shortening agents in baked products. Commercially, these are prepared by hydrogenation of oils, during which, some of the double bonds are isomerised into *trans* fatty acids from their *cis* configuration. *Trans* fatty acids have higher melting points and greater stability against oxidative rancidity than their *cis*-isomers and are important contributors to the functional properties of hydrogenated products. To meet the requirements of health-conscious consumers fats having a wide melting range which crystallize in the β' polymorphic form without the formation of *trans* fatty acids are needed [23].

Palm oil, because of its naturally β' tending nature, is favoured for shortening applications, such that it can impart stability to the emulsion, smooth consistency and provide good aeration properties [10].

3. Mechanical properties

When triacylglycerols are cooled from the melt to a temperature below their melting point, i.e., when they are supercooled, they undergo a liquid–solid transformation to form primary crystals with characteristic polymorphism. These primary crystals aggregate, or grow into each other, to form clusters, which further interact, resulting in the formation of a continuous three-dimensional network. The mechanical properties of a fat, can be influenced by all these levels of structure; however, most directly by the level of structure closest to the macroscopic world, namely the microstructure [24].

It is during crystallization that the template for the final physical properties of the resulting fat crystal network is created. Hence, the mechanical properties of a fat crystal network are determined by the different levels of structure, such as chemical composition, solid fat content (SFC), and crystal habit (polymorphism and microstructure). To study the mechanical properties of fat crystal networks, rheologic tests are used, which measure how the crystallized material responds to applied forces (stress) and deformations (strain) [18].

Foods are edible structures created as a result of the responses of proteins, polysaccharides, and lipids in aqueous media to different processing methods, such as thermal processing, homogenization, and other physical treatments. The processing operations to which foods are subjected affect their structure and microstructure. Most, if not all, of the responses are physical in nature. By definition, rheology is the study of deformation and flow of materials. In foods, measured rheological responses are those at the macroscopic level. However, they are directly affected by the changes and properties at the microscopic level. Fractal dimension has been used to characterize food particles in addition to microscopic and size distribution data. The fractal dimension can be estimated by several techniques such as viscoelastic behavior [25].

3.1. Rheology and texture

Rheology has been defined as the study of the flow and deformation of materials, with special emphasis being usually placed on the former. In flow, elements of the liquid are deforming resisted by viscosity. Solids when stressed creep, i.e. continue to deform very slowly over a very long time scale. In structured liquids there is a natural rest condition of the microstructure that represents a minimum-energy state. When these liquids are deformed, thermodynamic forces immediately begin to operate to restore this rest state. This kind of energy is the origin of elasticity in structured liquids. Alongside these elastic forces are the ever-present viscous forces that produce viscoelastic effects [26].

Rheological methods can be divided into small and large deformation rheology. *Small deformation rheology* does not cause structural damage to the sample. They are performed in the linear viscoelastic region (LVR), in which the stress is directly proportional to the strain. *Large deformation rheology* is based on the deformation of a sample at a constant rate to the point where the force exceeds the structural capacity of the sample, causing it to permanently deform and break [18]. Sometimes, oscillatory testing is referred to as small amplitude oscillatory testing because small deformations must be employed to maintain linear viscoelastic behavior. Many processes, such as mastication and swallowing, are only accomplished with very large deformations. Collecting viscoelastic data relevant to this type of problem involves testing in the non-linear range behavior [27].

A frequently used method of measuring linear viscoelastic response is oscillatory testing, i.e. applying an oscillating stress or strain as an input to the liquid and monitoring the resulting oscillatory strain or stress output. Oscillatory tests are performed over a range of frequency. Short times correspond to high frequencies, and long times relate to low frequencies. In a sine-wave-shaped input of either stress or strain the resulting sinusoidal strain or stress output is separated into solid-like response, which is in phase with the input, and a corresponding liquid-like response which is $\pi/2$ (i.e. 90°) out of phase with the input. The solid-like component at any particular frequency is characterized by the storage modulus, G' , and the liquid-like response is described by the complementary loss modulus, G'' . The behavior normally seen for typical viscoelastic liquids is an initial elastic response, thereafter, a delayed elastic response where the deformation rate becomes slower and slower, ending up as a very slow but steady-state deformation at the longest times, i.e. the material is in steady flow. The overall G' , G'' response of structured liquids is shown in Figure 4 [26].

G' expresses the magnitude of the energy that is stored in the material or recoverable per cycle of deformation, while G'' is a measure of the energy which is lost as viscous dissipation per cycle of deformation. For a viscoelastic material the resultant stress is also sinusoidal but shows a phase lag of δ radians when compared with the strain. The phase angle covers the range of 0 to $\pi/2$ as the viscous component increases. If G' is much greater than G'' , the material will behave more like a solid, i.e., the deformations will be essentially elastic or recoverable. The loss tangent, $\tan \delta$, is the ratio of the energy dissipated to that stored per cycle of deformation. When G'' is much greater than G' , the energy used to deform the material is dissipated viscously and the materials behavior is liquid like [25].

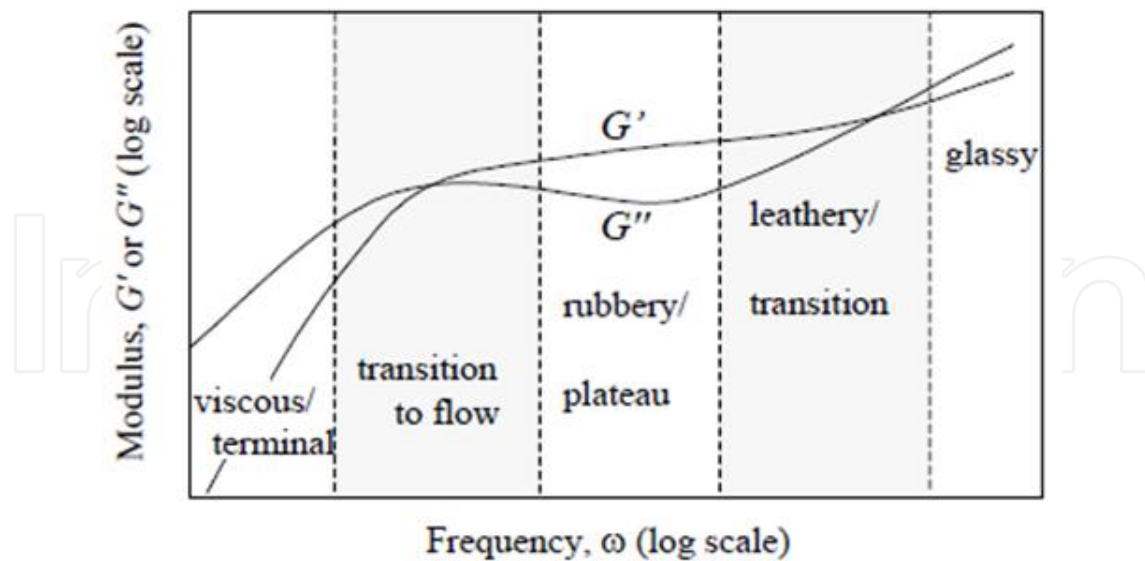


Figure 4. The various regions of an oscillatory test of structured liquids [26].

The penetrometry method and the two-plate compression method are large-deformation tests and are widely used to determine the yield stress or the firmness of a plastic fat. The large-deformation method has been widely used to study the physical properties of fat products, such as the spreadability of shortenings and the hardness of chocolate and milk fat, and the results have been found to correlate well with sensory tests [28].

Texture has been defined as the way in which various constituents and structural elements are arranged and combined into a micro- and macrostructure and this structure is externally manifested in terms of flow and deformation [29]. The structural elements of fats consist of solid fat crystals. They are suspended in liquid oil and when present in sufficient quantity form a three-dimensional network that imparts plastic properties to the fat. The external manifestations of this network structure include a number of physical and mechanical properties such as hardness, softness, spreadability, brittleness, shortening power, and aeration properties. The texture of fats is influenced by a number of factors, including the solids content, the fatty acid and triacylglycerol composition of the solids, the polymorphic behavior of the fat crystals, the size and shape of the crystals, the nature of the crystal network, mechanical treatment, and temperature history. Many of these factors are interrelated, making it difficult to establish the effect of each independently [30]. Crystallization usually results in harder materials with higher solid fat contents. In addition, microstructural differences must be taken into account when evaluating the functional properties of lipids. The possibility of different polymorphic forms must not be neglected either because it can influence the texture and sensory profile. The texture of plastic fats can be determined by three main methods such as: cone penetrometry, penetration by a probe, compression between parallel plates. The analyses and the evaluation of food texture are very important in food processing. Some of the attributes such as hardness and adhesiveness can be evaluated by texture analysis.

3.2. Fractal

Once the attraction forces have become larger than the repulsion, and also larger than Brownian motion, particles can remain together when they collide. The resulting aggregates or flocs have a very complex structure and most of the flocs do not have homogeneous internal structures. The center is usually denser than the outer regions; hence the mass does not change with the third power of the radius as in normal objects with constant density [31].

Many patterns in nature such as the geometry of coastlines, mountains, trees, and vegetables, for instance, cannot always be defined adequately by using the familiar straight lines, circles, conic sections, polygons, spheres, quadratic surfaces, etc. Fractal geometry was born out of this lack of geometrical tools. A geometric shape belongs to standard geometry when smaller and smaller portions of it become increasingly smooth. For example, a generic curve becomes a straight line, and a generic surface becomes a plane. Fractals are shapes whose roughness and fragmentation neither tend to vanish, nor fluctuate up and down, but remain essentially unchanged as one zooms in continually and examination is refined. Hence, the structure of every piece holds the key to the whole structure. Fractals are characterized by two types of symmetries: self-similar and self-affine. In self-similar each part is a linear geometric reduction of the whole, with the same reduction ratios in all directions. In self-affine, the reductions are still linear but the reduction ratios in different directions are different [32].

A fractal dimension is a powerful means of quantifying the structure of non-Euclidean objects by capturing the complexity of a structure's geometry in a single number. The challenge, however, is to give physical meaning to the number obtained [24].

The macroscopic rheological properties of the network are influenced by all levels of structure defined during the formation of the network, i.e. the structure of the individual triacylglycerols, the structure of the individual crystalline units formed, or the polymorphic nature of the network, and the microstructural level of structure. The microstructural aggregate or microstructural network present in fat crystal networks scale in a fractal manner in the range between the size of the individual particles composing the sample (microstructural elements) and the size of the microstructures. For colloidal aggregates and other fractal systems (such as fat crystal networks), fractal concept quantifies the way in which the mass of the sample/system increases with its size, according to the fractal dimension [33].

3.3. Fat crystal network

Early nucleation and crystal growth events lead to the formation of submicron primary crystallites from the melt. These crystallites associate into micron-range particles, which further aggregate into clusters, until a continuous three-dimensional network with voids filled with liquid fat is formed [18].

A structural hierarchy exists within fat crystal networks. Polymorphism has to do with different molecular packing arrangements of triacylglycerol molecules, at the nanostructural range, within the primary fat crystals. Once the primary fat crystals are formed, they aggregate, or grow into each other, to form fat crystal clusters (or aggregate), which in turn cross-

link to build up a 3-D fat crystal network. The shape of the fat crystal clusters can be spherulitic, feather-like, blade or needle-shaped. The size of fat crystal clusters can vary from several micrometers to more than 200 μm . Processing conditions can affect the size of the fat crystal clusters [28].

Fats are the main structural constituents of many food products including margarine, chocolate, butter and spreads. The sensory textural characteristics (i.e., spreadability, hardness, snap) of fat structured foods are dependent on their macroscopic rheological properties, which are a consequence of the structure of their underlying fat crystal network. This network arises from the interactions between polycrystalline fat particles, and provides the elastic component, or the solid-like behavior, of a plastic fat. The sensory properties of the fat-structured foods are dependent not only on the amount of solid fat crystals present and their polymorphism, but also their geometry and the spatial distribution of crystalline material [34].

The microstructure of fat crystal networks can be quantified by fractal dimensions, which can describes the combined effects of morphology and spatial distribution patterns of the crystal clusters in fat crystal networks. The usefulness in the quantification of the microstructure of fats using the concept of fractal dimension arises from the possibility of relating structure to physical properties [28]. The fractal model of fat crystal networks explains the scaling behavior of rheological properties of semi-solid fat products to their solid fat content by their microstructure, which can be quantified using fractal dimensions. In general, different microscopy fractal dimensions reflect different aspects of the micro-structure and thus have different physical meanings. An unambiguous agreement between physical fractal dimensions and microscopy fractal dimensions is required [25].

Fat crystal networks are statically self-similar, which means that the microstructure in a fat crystal network looks similar at different magnifications. Fractal structures are created by agglomeration, or clustering, of small particles to form a larger object in a random, iterative fashion under some constraint. In a similar fashion, fat crystal networks are built from clusters of polycrystalline particles (crystallites) that aggregate in a diffusionally limited, fractal fashion. Fractal mathematics have been used to relate the elastic properties of fat crystal networks to the spatial distribution of the network mass and to link crystallization kinetics and phase behavior to microstructure. The fractal dimension defines the cluster size and has been evaluated by rheology techniques. Rheology is the most common technique for the quantification of microstructure in fat crystal networks and utilizes the relationship of the shear storage modulus (G') to the volume fraction of network solid mass via the mass fractal dimension of the network [18].

The shape, size, and the strength of the fat crystal flocs making up the fat crystal network are always different. The weakest floc will become a flaw and acts as a stress concentrator. The elastic properties of the network depend on the number of connections between neighboring structural clusters, rather than on the amount of apparent solids. This implies that the connectivity of the networks increases with an increasing volume fraction of solids. An idealized view of the structure of a fat crystal network showing the one dimensional deformation of the links between crystal clusters [35]. In this same work, by using a modified

fractal model, which describes the increase of G' with SFC well, show the idea that the stress-carrying mechanism in fat crystal networks is heterogeneous, i.e. since real networks are not fully connected and that connectivity of networks increases with the volume fraction of solids, the load-bearing volume fraction of solids in real networks increases in an exponential fashion with the apparent volume fraction of solids.

4. Fat foods

Fats and oils are the raw materials for liquid oils, shortenings, margarines, and other specialty or tailored products that are functional ingredients in food products prepared by food processors and restaurants and in the home. Humans have used fats and oils for food and a variety of other applications since prehistoric times, as they were easily isolated from their source. Fats and oils found utility because of their unique properties. These ingredients were found to add flavor, lubricity, texture, and satiety to foods. They have also been found to have a major role in human nutrition. Fats and oils are the highest energy source of the three basic foods (carbohydrates, proteins, and fats), and many contain fatty acids essential for health that are not manufactured by the human body [2].

While vegetable fats were used originally as a cheaper substitute for milk fat the ability to specify the properties of vegetable fat has considerable advantages. This ability arises because of the science and technology available to the fat processing industry. Some vegetable fats used in foods are not tailor-made but are simply a vegetable fat of known origin and treatment. The commonest example is palm kernel oil (HPKO), which is often used in foods.

4.1. Chocolate products

Chocolate can be described as a suspension consisting of nonfat particles (sugar and cocoa solids and, eventually, milk powder particles) dispersed in cocoa butter as a continuous phase. Molten chocolates represent a dense blend of phospholipid-coated sucrose and cocoa particles in liquid fat. Milk chocolate usually contains about 12 g of cocoa mass, 19 g whole milk powder, 48.5 g sugar and, additionally, 20 g added cocoa butter per 100 g chocolate [36].

The characteristic flavor of chocolate has to be developed in several processing steps. During processing, the components are mixed, refined, and conched to attain desired rheological properties for a final defined product texture and melting characteristics. A conche is a scraped-surface mixer that optimizes flavor development and turns chocolate mass into a flowable liquid. Through shear and longitudinal mixing, acidic flavors and moisture in the cocoa mass are reduced. Upon entering the conche, not all sugar and cocoa particles will be coated with cocoa butter. Fat in the chocolate will be released from the agglomerated chocolate mass and spread to cover these particles so that they can flow easily. The final chocolate mass viscosity should be deemed optimal for the ensuing tempering [37].

Cocoa butter, which amounts to 25-36% in finished chocolate, is responsible for the smooth texture, contractability, flavor release, and gloss of the product. The fat phase is

the only continuous phase in chocolate, thus responsible for melting behavior and the dispersion of all other constituents. A careful tempering of the chocolate is necessary in order to obtain the fine crystals in the correct form (β -modification). Cupuassu fat, a similar cocoa butter fat, shows polymorphic behavior like cocoa butter (β form) and needs to be tempered like cocoa butter; at 24-25°C an α (alpha) form is present. The melting profiles of cocoa butter and cupuassu fat are similar as shown. At all temperatures, cocoa butter has a higher solid fat content than cupuassu fat. This suggests that cupuassu fat would be useful in filled chocolate manufacture as a softer filling fat compatible with cocoa butter. The fatty acid and triacylglycerol compositions of cupuassu fat in comparison with cocoa butter show that palmitic acid in cupuassu fat is present in much smaller amount (7.8%) than in cocoa butter (26.1%); stearic acid is about the same; oleic acid is higher in cupuassu. Particularly notable is the high amount of arachidic acid (20:0) in cupuassu fat. The triacylglycerol compositions reflect the fatty acid compositions, but give more useful information. Although cupuassu has a higher SOS content than cocoa butter, its contents of POP and POS are much lower reflecting its low level of palmitic acid. Total SOS-type triacylglycerols, i.e. POP+POS+SOS+SOA, is 57% in cupuassu and 83% in cocoa butter. Fractionation, as applied to fats such as shea and sal, would be needed to bring the total SOS-type content to the same as in cocoa butter. Fractionation could be used to modify cupuassu fat to make it more similar to cocoa butter for use as a CBE (cocoa butter equivalent), with 65% minimum of total SOS-type triacylglycerols [38].

Modified lipids are used in the majority of chocolate and confectionery applications, such as chocolate compounds, filling fats in pralines, aerated products and cold products such as ice cream toppings. Production economics is often related to price, speed of production and equipment requirements, which in turn are related to the raw materials and their ability to crystallize rapidly.

The quality is related to the capacity of the fat to remain stable in terms of appearance, texture and taste; and the sensory properties can briefly be described as appearance, smell, taste and the role that fat plays in mouth feel with regard to texture and melt off properties. In chocolate industry fat bloom is still a problem. It modifies (shortens) the shelf life of the end products and makes life difficult for product development. Fat migration is one of the causes of bloom, but it will also soften the products during storage [39].

In chocolate industry, for processing and texture reasons, however, it is not possible to reduce the level too much below 25%. This is insufficient to make a low calorie claim on the product, so two manufacturers have produced fats that melt like cocoa butter but have a lower calorific value. Like lauric fats they are incompatible with cocoa butter and so the products have to be made with cocoa powder [36]. Some fats go into confectionery as a component of other ingredients. The common example is nuts, which contain fats, often of types such as lauric or unsaturated fats. These fats are sometimes the origin of spoilage problems.

Studies correlating chocolate composition and textural or rheological properties are commonly found due to the source of new fat or cocoa butter replacers which strongly affect rheological parameters on chocolate manufacture and final product texture. According to that, adaptations on manufacturing scale have to be done in order to keep the desirable sen-

sory characteristics in the final product. Rheology is a useful feature on setting those issues. Several works have been conducted to study and understand rheological properties of chocolates. The various fats used in chocolate can contain different levels of trisaturated triacylglycerols. Since these can crystallize out early in the tempering process, they can, in some instances, have an effect on the rheology of the chocolate. Six basic source oils are permitted as non-cocoa vegetable fats (CBE - Cocoa Butter Equivalent) in chocolate throughout European Union - palm oil, shea oil, illipe butter, sal oil, kokum gurgi, and mango kernel oil. Among these six oils, four (palm, shea, sal, and mango kernel) usually have to undergo some form of fractionation process to concentrate the SOS type of triacylglycerol necessary for equivalence to cocoa butter. Palm oil is even more complicated since it contains a significant quantity of trisaturated triacylglycerols which also have to be removed [40].

4.2. Ice cream

Ice cream has been identified as three component foam made up of a network of fat globules and ice crystals dispersed in a high viscosity aqueous phase. The composition of ice cream varies depending on the market requirements and processing conditions. Although the quality of the final product depends largely on the processing and freezing parameters, the ingredients also play an important role. The physical structure of ice cream affects its melting rate and hardness, although the specific relationships have not all been worked out. Structure development in ice cream often is attributed to the macromolecules present in the ice cream mix - milk fat, protein, and complex carbohydrates. Milk fat interacts with other ingredients to develop the texture, mouthfeel, creaminess, and overall sensations of lubricity. Typically, ice cream contains 10 to 16% fat and its type and amount influence the characteristics of the resultant products by affecting their rheological properties. The fat content can influence the size of the ice crystals. Fat globules could mechanically impede the ice crystal growth. Since each type of fat exhibits a specific polymorphism function of its triacylglycerol composition, the thermal behavior of fats during ice cream processing should influence the physicochemical properties of the intermediate and final products [41].

A typical ice cream formulation has fat (7-15%), lactose (5-7%), other sugars (12-16%), stabilizers, emulsifiers and flavours (0.5%), total solids (28-40%), water (60-72%), milk protein (4-5%). Fat performs several functions in ice cream: it helps to stabilize the foam, it is largely responsible for the creamy texture, it slows down the rate at which ice cream melts and it is necessary to deliver flavour molecules that are soluble in fat but not water. The major sources of fat used in industrial ice cream production are butterfat, cream and vegetable fat [42].

Ice creams are metastable systems created from an emulsion o/w employing several unit operations: mixing, heating, cooling, freezing, aerating and packaging. While the ingredients combination is responsible by chemical characteristics, a sophisticated microstructural arrangement constituted by fat globules, ice crystals and air bubbles supported in a highly viscous matrix dictates mechanical, thermal and sensorial properties.

There are many factors within the microstructure of products, which determine the rheological properties, such as colloidal interactions between dispersed components, the junctions between structural elements, the properties of these elements, the interfacial behavior be-

tween phases, the rheology, and structure of individual component phase. In order to improve the quality of this very appreciated foodstuff, ingredients research and their impact on formulations are very desirable. In [43] was investigated the potential of a chemically modified polysaccharide (N-succinil chitosan hydrogel) when applied as structuring agent in colloidal systems. It was found that the mixes resulting by combination among chitosan and palm fat presented good characteristics; the enormous structuring power presented by this biomolecule can be very useful to elaborate low-fat formulations with good textural properties. Moreover, taking in account the physiological activity, it can be employed in order to promote best nutritional quality in foods; this biopolymer and their derivatives, can be extensively explored, since appear do not has limitations in its potentialities.

In [41] was found in study that the replacement of hydrogenated vegetable fat by palm fat caused changes in melting ranges of formulations. Higher melting rate was observed by combination between palm fat and fructose syrup. In addition to effects expected on melting behavior and solids content, sugar blends employed in this study affected the air incorporation. There is consense that greater air content increase the melting resistance. However, despite to lower overrun, ice creams made with fructose syrup melted more slowly. Thus, the levels of air added into the products not allow safe conclusions about the influence of this parameter on physical behavior of assessed ice creams in this study. In [44] was evaluated also the influence of the substitution of hydrogenated fat in the manufacture of ice cream formulation with palm fat through rheology analysis, and compare the results obtained with the melting test. The rheological and the melting tests showed a better response from the ageing process, and a better formed structure with the formulation produced with hydrogenated fat. It was suggested that formulations produced with palm fat suffers a poorer partial coalescence by its crystallization profile and less membrane destabilization by the emulsifiers.

In another study was evaluated the influence of the substitution of hydrogenated fat in the manufacture of ice cream formulation with cupuassu fat through rheology analysis, and compare the results obtained with the melting test. The rheological tests showed similar response from the ageing process to both formulations, and the melting tests showed a slower meltdown of the structure with the ice cream produced with cupuassu fat. The results obtained demonstrated that cupuassu fat is a good substitute for hydrogenated vegetable fat for using in ice cream formulations [45].

4.3. Bakery

The functionality of fats in bakery products can be explained as: development of the structure; lubrication; aeration; heat transfer; moisture retention; improved shelf-life, volume, texture and flavor. In some cases the function of a fat can be either partially or completely replaced by some other ingredient, typically an emulsifier.

Fats shorten the texture of baked products by preventing cohesion of gluten strands during mixing, hence the term shortening. All-purpose shortenings are used primarily for cookies but are also common ingredients in cakes, breads, and icings and are also used for frying applications. The quality of cakes and icings is highly dependent upon aeration; therefore, a

variety of very specialized shortenings has been developed over the years to satisfy that demand. High ratio shortenings (containing mono and diglycerides), designed primarily for cakes, began to appear in the '30s. Fluid cake shortenings were commercialized in the '60s and offer many advantages including pumpability, ease of handling and the option of bulk delivery and storage [46].

Cake is a baked batter made from wheat flour, sugar, eggs, shortening, leavening agents, salt, nonfat dry milk, flavors, and water. Cake batters are essentially a 'foam', that is a system in which air bubbles are trapped and held in an aqueous phase. The main function of fat in cake making is to assist with the incorporation of air into the batter during mixing, and the air bubble size and stability. High-ratio cakes, rich in sugar and fat, are extensively used in the baking industry [47].

Margarine has always had the advantage over butter in that the properties of the product can be tailored to give the best performance in a particular system. For puff pastry, i.e., specialized margarines are easier to work with than butter. Various bakery margarines are manufactured to meet the technical requirements of particular uses.

The effect of different fats and margarines on the physical properties of cakes was investigated. The low *trans* fat suggested: greater volume and firmness; resilience comparable to hydrogenated fat; elasticity and chewiness were comparable to other formulations, as well the color parameters of the crumbs [48].

Textural properties are important quality parameters for this type of product. Physical and structure changes during aerated batters processing may alter their performance during baking or the quality of the final product. It is possible to test materials with particles and fiber in suspensions, since flushing effects may reduce sedimentation problems. In [49] was examined the influence of different types of fats (hydrogenated fat, margarine and vegetable oil) in formulation of cake batter, evaluating textural properties by Herschel-Bulkley equation using back extrusion analysis; and it were observed values close in all parameters to samples prepared with margarine and hydrogenated fat. It can be mentioned the break point values could be consider by the industry as an important parameter, pointing the need of less energy in their processes of pumping, i.e.

4.4. Food emulsions

4.4.1. Mayonnaise and salad dressing

Mayonnaise and salad dressing are emulsified, semi-solid fatty foods that by federal regulation must contain not less than 65% and 30% vegetable oil, respectively, and dried whole eggs or egg yolks. Salt, sugar, spices, seasoning, vinegar, lemon juice, and other ingredients complete these products. Pourable and spoonable dressings may be two phase (e.g., vinegar and oil) or the emulsified viscous type (e.g., French). There is a great variety of products available of varying compositions with a wide range in their oil content. Salad oils exclusively are used for dressing products; typical choices include soybean, canola and olive oils [46].

Emulsion is a thermodynamically unstable system due to flocculation, creaming, coalescence, phase inversion and Ostwald rippling. Emulsifier is a surfactant which can stabilize the emulsion by absorption at the interface, thereby lowering the interfacial tension. It is usually used to improve the emulsion stability. Proteins and polysaccharides are often applied in emulsion as emulsifier. Proteins are usually used for their surfactant and gelling properties to improve the textural characteristics and stability of emulsion, while polysaccharides are usually added to increase the viscosity or to obtain a gel-like product. It was studied the impact of the use of a biomaterial (N-succinil chitosan hydrogel) in elaboration and structuration of food emulsion, and in substitution of a part of the oil phase. Chitosan showed to be a versatile ingredient since that was capable to modify the rheological properties, acting as emulsifying agent, besides its already known antimicrobial and nutritional qualities [50].

4.4.2. *Margarine*

Margarine and spreads are prepared by blending fats and/or oils with other ingredients such as water and/or milk products, suitable edible proteins, salt, flavoring and coloring materials and Vitamins A and D. Margarine must contain at least 80% fat by federal regulation, however, "diet" margarines and spreads may contain 0-80% fat. These products may be formulated from vegetable oils and/or animal fats, however, the vast preponderance are all vegetable. Non hydrogenated oils typically represent the majority of the fat phase. Lesser amounts of partially hydrogenated fats, that are naturally semisolid at room temperature, and/or hard fractions of certain fats are added to the blend as required to deliver the desired structure and melting properties [46]. At the moment, interesterification technics have been employed to produce tailor fats. Margarine originated as a substitute for butter. The big advantage of margarine is that as a manufactured product the properties can be tailored to suit a particular use.

An acceptable margarine must be a soft plastic at room temperature; the ratio of solid or crystalline fat to liquid oil in the mixture must be such that when the fat crystals are of the proper size and well dispersed, the mass will offer some resistance to deformation and separation of solid and liquid fats will be negligible; all the fat crystals must melt completely at body temperature and leave a pasty sensation in the mouth; the fat crystals must not melt abruptly [51].

5. Prospective

The major brands are today sold all over the world. The economic impact of any bad image on these super brands has led the major companies to focus on brand image. The increase in obesity has focused on health aspects of foods in general but also on chocolate and confectionery products. Fat replacers of the future will need to meet some important criteria, including reducing or replacing the target fat effectively, being available at a cost appropriate to the benefits provided, and being safe and legal with no appreciable side effects [39, 52].

Author details

Suzana Caetano da Silva Lannes and Rene Maria Ignácio

*Address all correspondence to: scslan@usp.br

Biochemical-Pharmaceutical Technology Department, Pharmaceutical Sciences Faculty, Sao Paulo University, São Paulo, Brazil

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