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Advances in Lipids Crystallization Technology

Maria Aliciane Fontenele Domingues, Ana Paula Badan Ribeiro,
Theo Guenter Kieckbusch, Luiz Antonio Gioielli, Renato Grimaldi,
Lisandro Pavie Cardoso and Lireny Aparecida Guaraldo Gonçalves

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1. Introduction

In recent years, the industrial sector of oils and fats has become an important area of research and technological development. The number of studies related to the physical properties of oils and fats has been increasing; these properties are broadly the melting and crystallization behavior and the crystalline and oxidative stability of oils and fats.

The crystallization behavior of lipids has important implications in the industrial processing of food products whose physical characteristics depend largely on fat crystals. Such products include chocolates, margarines, spreads, fats for confectionery and bakery, dairy products, and commonly used shortenings [1]. Meanwhile, crystallization is the most important physical problem of oils and fats [2], particularly problems such as unwanted polymorphic transitions, oil exudation, the development of fat bloom, formation of crystalline agglomerates, and fatty bases with a maximum solid fat content or incompatibility of induction periods with certain industrial applications. Thus, recent research has focused on understanding the phenomena involved in the crystallization of lipids in an attempt to achieve effective solutions to stabilize or modify this process, depending on the nature of the raw material and its industrial application. To that effect, the use of emulsifying agents as crystallization modifiers has marked the trend of research in the oils and fats field. In the past, studies were based on the effect of emulsifiers on the crystallization of pure triglycerides or model systems [3, 4, 5], while recent research has focused on the effect of emulsifiers on the crystallization properties of different types of fats such as milk fat [6, 7, 8], low-trans fats [9, 10], palm oil and its fractions [11, 12], cocoa butter [13], in the crystallization of emulsions [14, 15], and production of organogels, which constitute the structuring oils of emulsifiers [16]. While studying the effects of emulsifiers in fatty systems is of great interest for the improvement of industrial bases, particularly

with respect to fat for use in chocolate, confectionery, and baking, there is limited research on the role of these compounds as crystallization modifiers of natural and commercial fats [17].

Crystallization of lipids is a serious problem in the food industry with respect to actual industrial processes and post-crystallization events. The crystallization issue presents additional aggravating considerations related to climatic differences between countries and the transport and storage conditions imposed by long distances between producing regions and final distribution regions. Thus, there is a need for appropriate solutions for processes involving crystallization and stabilization of raw materials of significant industrial relevance, such as palm oil and fractionated and interesterified fats, which are now replacing partially hydrogenated fats (or trans fats) in most industrial applications. Therefore, the topic discussed in this chapter is highly relevant to the oils and fats production sector.

2. Oils and fats

Edible oils and fats are essential nutrients of the human diet, playing a vital role in providing essential fatty acids and energy. Chemically, natural oils and fats consist of multi-component mixtures of triacylglycerols (TAGs), which are glycerol esters and fatty acids. Additionally, polar lipids (minority lipids) such as diacylglycerols (DAGs),monoacylglycerols (MAGs), free fatty acids, phospholipids, glycolipids and sterols are found solubilized in the triacylglycerol matrix. The triacylglycerol composition determines the physical properties of oils and fats, affecting the structure, stability, flavor, aroma, storage quality, and sensory and visual characteristics of foods [18].

The physical properties of an oil or fat are of fundamental importance to determine its use. This is particularly true for a large quantity and variety of oils and fats used in various forms, including foods. The difference between the words "oil" and "fat" refers to a fundamental physical property, the fluidity or consistency at room temperature. The components of fat characterize it as a material composed of an intimate mixture in the liquid and solid phases, and its physical state can vary from a viscous fluid to a solid or brittle plastic [19].

3. Physical properties of oils and fats

3.1. Crystallization behavior

Plastic fats consist of a lattice network in a continuous oil matrix. The crystallization process is a spontaneous ordering of the system, characterized by the total or partial restriction of movement caused by physical or chemical links between the triacylglycerol molecules. Differences in crystal shapes result from different molecular packings. A crystal, therefore, consists of molecules arranged in a fixed pattern known as a lattice. Its high degree of molecular complexity allows the same set of TAGs be packaged into several different and relatively stable structures [20].

Crystallization of fats determines important properties of foods, including: (i) the consistency and plasticity of fat-rich products such as butter, margarine and chocolate during the stages of production and storage; (ii) sensory properties such as the melting sensation in the mouth; (iii) physical stability with respect to the formation and settling of crystals, oil exudation and coalescence of particles and emulsions; and (iv) visual appearance, for example the shininess of chocolates and toppings [21]. In most foods, isolated crystallization of TAGs is considered the event of greatest importance, although the crystallization of minority lipids such as DAGs, MAGs and phospholipids plays a fundamental role in the quality of various products [22].

3.1.1. Crystallization mechanism of the lipids

Crystallization is generally divided into four distinct phases. Initially, in order to obtain the formation of crystals from the liquid state, the system must reach the supersaturation zone, in which there is a driving force for crystallization. Once the appropriate driving force to overcome the energy barrier for crystallization is reached, nucleation occurs and molecules in the liquid state join together to create a stable nucleus. After the formation of stable nuclei, a rapid transition to the next stage of crystallization occurs, crystal growth, i.e., during which additional molecules (or growth units) are incorporated into the crystal lattice, decreasing the driving force of supersaturation. Unless restricted by a kinetic constraint, growth continues until the system reaches equilibrium, at which the driving force for crystallization approaches zero and the maximum volume of the crystal phase is obtained [23].

3.1.2. Nucleation

According to Boistelle [24], nucleation involves the formation of molecule aggregates that exceed a critical size, and are therefore stable. Once a crystal nucleus has formed, it begins to grow due to the incorporation of other molecules from the adjacent liquid layer that is continuously filled by the supersaturated liquid surrounding the crystal [24].

A crystal nucleus is the smallest crystal that can exist in solution at a given temperature and concentration. The formation of a nucleus from the liquid phase, i.e., the nucleation process, requires the organization of molecules in a crystalline lattice of critical size after overcoming an energy barrier. The mechanisms of nucleation are generally classified as primary nucleation, which can be homogeneous or heterogeneous, and secondary nucleation. It is currently suggested that nucleation occurs via a two-step process. Molecular oscillations in the liquid phase lead to local organization of molecules into amorphous clusters (instead of crystal embryos, as postulated by classical nucleation theory – Gibbs, 1800), which then aggregate to form an amorphous cluster of critical size. This formation of amorphous aggregates is the first step in nucleation. At some point the molecules in the cluster are transformed into a crystalline structure, which is the second step for the formation of a stable nucleus. The combination of these two events characterizes the induction time before the onset of visual nucleation. This type of nucleation, however, rarely occurs under the conditions of industrial processes. In practice, nucleation is usually dominated by the heterogeneous mechanism in the majority of systems, where external surfaces or catalytic sites, such as molecules of different composition, are used to reduce the energy barrier. Although the exact mechanism of heterogeneous

nucleation is not yet fully elucidated, the phenomenon can be described as the result of interactions between the solid particle and the supersaturated fluid, causing the local ordering of molecules for formation of the nucleus. Secondary nucleation is the formation of a new nucleus in the presence of existing crystals, which may occur if microscopic crystalline elements are separate from an already formed surface, thus resulting in crystal fracture into small stable nuclei [22, 23, 25, 26].

When the nuclei formed achieve favorable dimensions, these elements become crystallites whose growth depends not only on external factors (supersaturation, solvents, temperature, impurities), but also internal factors (structure, connections, defects). Consequently, the crystal growth rate can vary by several orders of magnitude. Growth occurs by binding of molecules to a crystalline surface. At the same time, molecules are also detached. There is a continuous movement of molecules on the crystal surface, and the result of these processes determines the rate of growth, which is directly proportional to subcooling and varies inversely with the viscosity of the system [21]. Although nucleation and crystal growth are often considered separate events, they are not mutually exclusive. Nucleation also occurs as crystals grow from existing nuclei [27].

3.1.3. Recrystallization

Recrystallization was defined by Fennema [28] as any change in the number, size, shape, orientation or perfection of the crystals after completion of initial solidification.

The basic mechanism of the recrystallization process is size-dependent equilibrium (melting temperature or solubility) documented by the Gibbs-Thomson effect. Small crystals, due to the small radius of curvature of the surface, are slightly more soluble or have a slightly lower melting point than larger crystals. Over time, these differences promote the disappearance of small crystals and growth of larger crystals. These changes generally occur without a change in volume of the crystalline phase, and are driven by the difference in thermodynamic equilibrium based on the size of the crystals. These crystals occur slowly at a constant temperature, but their presence increases with temperature swings as the phenomenon referred to as Melting-Recrystallization becomes dominant. When the temperature rises during a temperature cycle, the crystals melt or dissolve to maintain phase equilibrium. The small crystals, which are less stable, disappear first. When the temperature starts to decrease during the temperature cycle, the volume of the crystal phase increases, but only by growing and without the formation of new nuclei. The mass of small crystals that melted is redispersed among the larger crystals. As the average size of the crystals increases, the number of crystals decreases as a result of these thermodynamic effects. Thus, a dispersion of many small crystals tends to minimize the surface energy (and surface area) by recrystallization [23, 29].

The final stage of crystallization in foods occurs during storage, and a population of crystals undergoes a recrystallization step, reaching a more broad equilibrium state. This phenomenon is of primary concern during storage of foods, and is responsible for changes to the texture of ice cream, fat bloom in chocolates and toppings and exudation of oil in products rich in fat. In lipid systems, the recrystallization process involves changes to the internal arrangement of the crystalline structure via polymorphic transformation [30].

3.1.4. Crystallization kinetics

Crystallization kinetics intensively influences the final structure of fats and shows to be closely related to their rheological and plasticity properties. When monitoring the formation of the solid crystalline material with respect to time it is possible to verify the nature of the crystallization process. Characterization of crystallization kinetics can be performed according to the induction time (τ_{SFC}) or the nucleation period (relative to the beginning of crystal formation) and the maximum solid fat content-SFC_{max}. The induction time reflects the time required for formation of a stable nucleus of critical size in the liquid phase [31]. As a definition, the τ_{SFC} is the time required for obtaining one crystalline nucleus per unit volume. The τ_{SFC} generally increases with increasing isothermal crystallization temperature and decrease of the sample melting point. Another useful parameter for evaluating isothermal crystallization is the crystallization stability time (t_{cs}), defined as the total time for stabilization of the solid fat content at a given temperature. This parameter consists of the sum of the time characteristics for nucleation and crystal growth [32].

The model most widely used to describe the kinetics of isothermal phase transformation is the Avrami model, developed in 1940, which relates the kinetics determined experimentally with the form of growth and final structure of the crystal lattice [33]. The Avrami equation gives an indication of the nature of the crystal growth process and is given by

$$\frac{SFC(t)}{SFC(\infty)} = 1 - e^{-kt^n} \, , \tag{1}$$

where *SFC(t)* describes the solid fat content (%) as a function of time, *SFC(∞)* is the limit of the solid fat content when time tends to infinity, k is the Avrami constant (min^{-n}), which takes into account both nucleation and growth rate of the crystals and n is the Avrami exponent, which indicates the mechanism of crystal growth [27]. The crystallization half-life ($t_{1/2}$) reflects the magnitude k and n according to the relationship

$$t_{1/2} = \left(\frac{0.693}{k} \right)^{1/n} \, . \tag{2}$$

Currently, the most common analytical technique for the investigation of crystallization kinetics of fats is nuclear magnetic resonance (NMR). However, various analytical techniques such as differential scanning calorimetry (DSC), polarized light microscopy (PLM), as well as rheological and turbidimetric techniques can be successfully employed. Understanding of the phenomena involved in crystallization kinetics is improved when considering combined use of various instrumental methods [34].

3.1.5. Polymorphism

Long-chain compounds, such as fatty acids and their esters, may exist in different crystal forms. Solids of the same composition which may exist in more than one crystal form are called polymorphs. Polymorphism can be defined in terms of the manifestation ability of different cellular structures, resulting from different molecular packings. The crystal habit is defined as

the crystal shape. From a crystallographic perspective, the habit reflects the growth direction within the crystal, while morphology outlines the set of faces determined by the symmetrical components of the crystal. This distinction allows crystals of the same morphology to present different crystal habits [26].In fat, crystals are solids with atoms arranged in a regular three-dimensional pattern. A cell is the repeating unit that makes up the complete structure of a given crystal. A sub-cell, in turn, is the smallest structure in the real unit of the cell, defined as the mode of transverse packing of aliphatic chains in the TAGs. The polymorphic forms of a fat are identified based on their sub-cell structure [24]. In lipids three specific sub-cell types predominate, referring to the polymorphs α, β' and β, according to current polymorphic nomenclature (Figure 1). The α form is metastable with hexagonal chain packing. The β' form has intermediate stability and orthorhombic perpendicular packing, while the β form has greater stability and triclinic parallel packing. The melting point increases with increasing stability ($\alpha \rightarrow \beta' \rightarrow \beta$), as a result of differences in the molecular packing density [35].

The polymorphic nature of the TAGs is well established. It is also well-known that the mixing of different fatty acid fractions in a TAG produces a more complex polymorphic behavior. Thus, saturated monoacid TAGs present simple polymorphism, followed by TAGs with mixed saturated fatty acids. The mixed saturated/unsaturated fatty acids exhibit more complex polymorphisms [36]. TAGs typically crystallize in the α and β' forms first, although the β form is most stable. This phenomenon is related to the fact that the β form has a higher free energy of activation for nucleation. Polymorphic transformation is an irreversible transformation process of the less stable form to the more stable form (transformation of the monotrophic stage), depending on the temperature and time involved. At constant temperature, the α and β' forms can transform, as a function of time, to the β form via the liquid-solid or solid-solid mechanisms [37]. The transformation velocity is dependent on the degree of homogeneity of the TAGs. Fats with low variability of TAGs quickly transform into the stable β form. Fats which consist of a random distribution of TAGs can present the β' form indefinitely. Additionally, factors such as formulation, cooling rate, heat of crystallization and degree of agitation affect the number and type of crystals formed. However, because fats are complex mixtures of TAGs, at a given temperature the different polymorphic forms and liquid oil can coexist [1].

Fats with a tendency to crystalize in the β' form include soybean, peanut, canola, corn and olive oil, as well as lard. In contrast, cotton and palm oils, milk fat and suet tend to produce β' crystals that commonly persist for long periods [21]. In particular, for cocoa butter six polymorphic forms are verified as a result of its unique triacylglycerol composition, wherein symmetrical monounsaturated TAGs predominate. The characteristic nomenclature of cocoa butter polymorphs are based on the roman numeral system (I to VI), where the I form is the least stable and the V form is associated with the desirable crystalline habit in chocolates, which may transform during storage into the VI form, which presents improved stability. However, combinations of this nomenclature with Greek nomenclature are typically encountered, where the forms V and VI are recognized as βV and βVI [38, 39].

The crystal structure of fats is important for the formulation of shortenings, margarines and fat products in general, since each crystal shape has unique properties with respect to plasticity, texture, solubility, and aeration. Fat with crystals in the β' form present greater functionality,
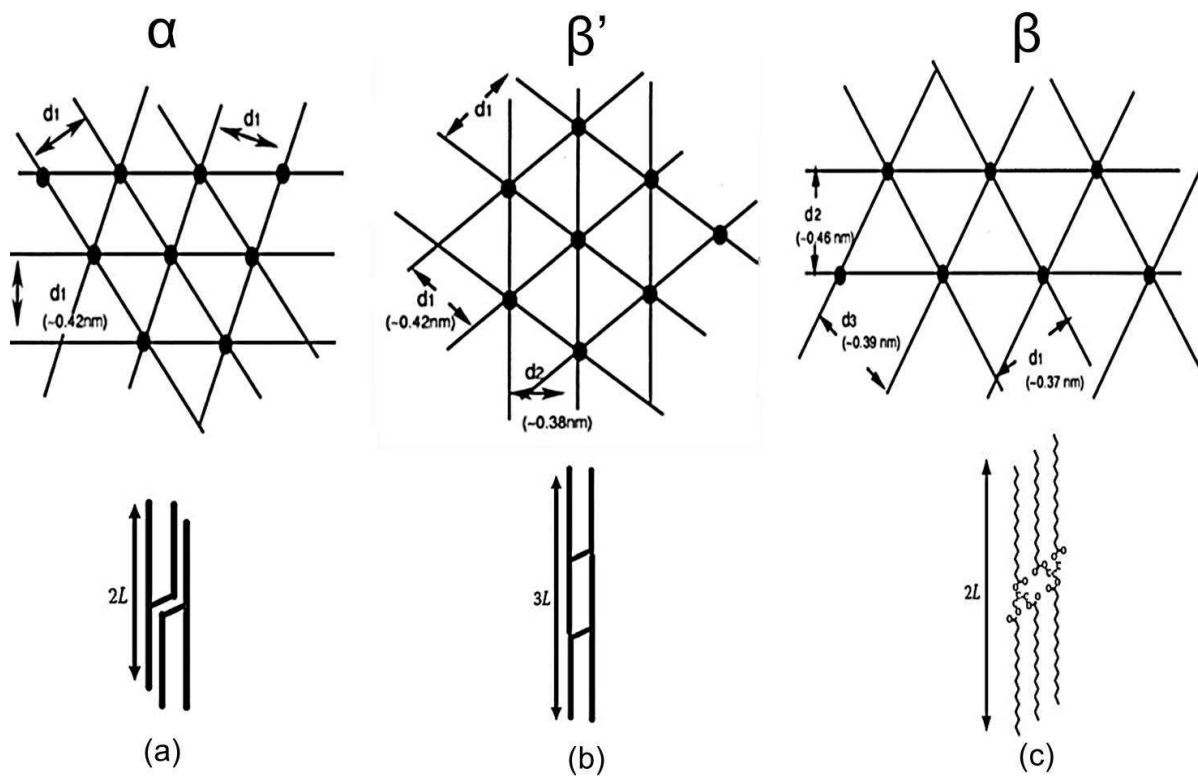
Figure 1. Spatial projections of the crystalline forms α, β 'and β. Packings: (a) H: hexagonal; (b): orthorhombic; (c) T: triclinic [40].

because they are softer and provide good aeration and creaminess properties. Therefore, the β' form is the polymorph of interest for the production of fat-rich foods such as margarine and confectionary and baking products. For the production of chocolates with good physical and sensory characteristics the βV form is the desirable polymorph, since it is associated with properties such as brightness, uniformity, snap characteristic and improved shelf life [18].

X-ray diffraction is an analytical technique used to identify the polymorphism of crystals by determining the dimensions of the crystalline unit and sub-cells. Due to different geometrical configurations, polymorphs diffract x-rays at different angles. In fats, high diffraction angles correspond to short spacings (distances between parallel acyl groups in the TAG) of sub-cells and allow for verifying the different polymorphs [41].

3.1.6. Microstructure

The lipid composition and crystallization conditions influence the crystal habit, i.e., different crystal morphologies are possible. Crystals aggregate into larger structures forming a lattice, which characterizes the microstructural level of a fat. The microstructure concept includes information regarding the state, quantity, shape, size, and spatial and interaction relationship between all components of the crystal lattice and has tremendous influence on the macroscopic properties of fats [42].

According in [43], the microstructural structure or meso-scale of a crystalline lattice for a fat may be defined as the set of structures with dimensions between 0.5μm and 200μm. Its quantification is achieved primarily by visualization of its geometry. Structural levels in a typical crystal lattice are defined when the fat crystallizes after its complete fusion. Like nanostructural elements (0.4-250nm), TAGs crystallize in specific polymorphic states. Most tags crystallize as spherulites, which implies that crystal growth occurs radially. The formed crystals grow to dimensions of 1 to 4 μm and then combine to form agglomerates (larger than 100μm) in a process governed by mass and heat transfer. The aggregation process continues until a continuous three-dimensional network is formed from the combination of these microstructures, trapped in the liquid fat phase [44]. This structural hierarchy has been recognized by several researchers. However, the arrangement of molecules in the crystalline state also depends on factors such as the cooling rate, crystallization temperature and stirring speed, if necessary [45].

Crystal growth can occur in one, two or three dimensions, characterizing the formation of needle, disk, or spherulite-shaped crystals, respectively [46], and these shapes can be predicted from the results shown by the value of the Avrami exponent (n) (Table 1). According in [47], the application of fats in food products requires that the average diameter of the crystals is less than 30μm to avoid a sensation of grittiness in the mouth.

Avrami exponent (n)	Type of crystal growth	Expected nucleation
3+1 = 4	growth of spherulites	sporadic nucleation
3+0 = 3	growth of spherulites	instantaneous nucleation
2+1 = 3	growth of disks	sporadic nucleation
2+0 = 2	growth of disks	instantaneous nucleation
1+1 = 2	growth of rods	sporadic nucleation
1+0 = 1	growth of rods	instantaneous nucleation

(SHARPLES, 1966) [48]

Table 1. Values of the Avrami exponent (n) for different types of crystal nucleation and growth.

Another factor that characterizes the formation of the microstructural network of fats is the fractal dimension. The fractal dimension is a parameter that describes the spatial distribution of the mass within the crystal lattice [44]. Fractal geometry was proposed by Benoit Mandelbrot (1982) as a method for quantifying natural objects with a complex geometrical structure which challenged quantification by regular geometric methods (Euclidean geometry). In classical Euclidean geometry, objects have integer dimensions: the reader would be familiar with the reasoning that a line is one-dimensional, a plain a two-dimensional object and the volume of an object is three-dimensional. Thus, Euclidean geometry is suitable for measuring objects that are ideal, or regular. One can imagine that if enough twists are placed on a line or a plane, the resulting object can be classified as an intermediate between a line and a plane. The dimension

of such an object is fractional (i.e., between 1 and 2 or between 2 and 3) and such an object can be classified as a fractal object, based on the fact that instead of presenting a Euclidean dimension (integer), it has a fractional dimension [49]. One of the most important characteristics of fractal objects is their similarity, in other words, fractals objects look the same in different magnitudes, at least in a certain range of scales.

Most scientific research on crystallization of fats has been directed towards establishing relationships between lipid composition or polymorphism and macroscopic properties of fats, without in-depth consideration of the microstructure of the crystal lattice, which can lead to failures in predicting the macroscopic properties [50]. In Marangoni and Rousseau [51] investigated the possibility that the solid fat content and/or polymorphic shape of the crystals is not determinant for the mechanical properties of mixtures containing milk fat with canola oil, but instead the macroscopic structure of the crystal lattice in the liquid oil matrix. From the study of fractal dimensions and the application of this theory to the rheological study of milk fat with canola oil moistures, it was observed that the fractal dimension (D_b) was the only "indicator" in accordance with the associated changes to the rheology of the product resulting from interesterification. Traditional physical indicators, such as polymorphism and solid fat content, failed to demonstrate the expected changes. Thus, the study confirmed the importance of the fractal dimension, a fundamental indicator of the crystal lattice capable of explaining changes in rheology of fats not attributed to other measurable properties of the network [49]. According in [27], systems with higher fractal dimension values demonstrate higher packing orders of the microstructural elements.

One of the methods most used for calculating the fractal dimension is the box counting method, where grids with length l_i are placed on the micrographs of the crystalline lattice of a fat obtained by the polarized light microscopy technique. Any lattice containing particles above a threshold value is considered an occupied lattice (solid). The number of occupied grids N_i of side length l_i is counted. This process is repeated for grids with different lateral lengths. The fractal dimension of box counting, D_b, is calculated as the opposite slope of the linear regression curve for the log-log graph of the number of occupied grids N_b versus the lateral length l_b, given by

$$D_b = -\frac{\Delta \ln N_b}{\Delta \ln l_b}.$$
(3)

To reduce errors, the grids with extreme sizes should be exempted from the calculation [52]. Polarized light microscopy (PLM) is the most widely used technique for visualization of microstructural network of fats and has been applied so as to explain the differences in texture of fat mixtures, showing crystalline types and morphological alterations in crystal growth [53].

4. Control of crystallization

Control of crystallization to prevent crystal growth or to achieve the desired crystalline attributes is crucial for obtaining high-quality products with long useful life. Understanding

the principles that underlie the crystallization phenomena is necessary to achieve this control [23]. Figure 2 presents a schematic of the crystallization process, storage of fats and associated mechanisms.

The behavior of crystallization, polymorphic transformation and microstructure of a fat is due to a combination of individual physical properties of each TAG and phase behavior of different TAG mixtures. In general, the specific composition of a fat is one of the most important factors for final development of the crystal structure [54].
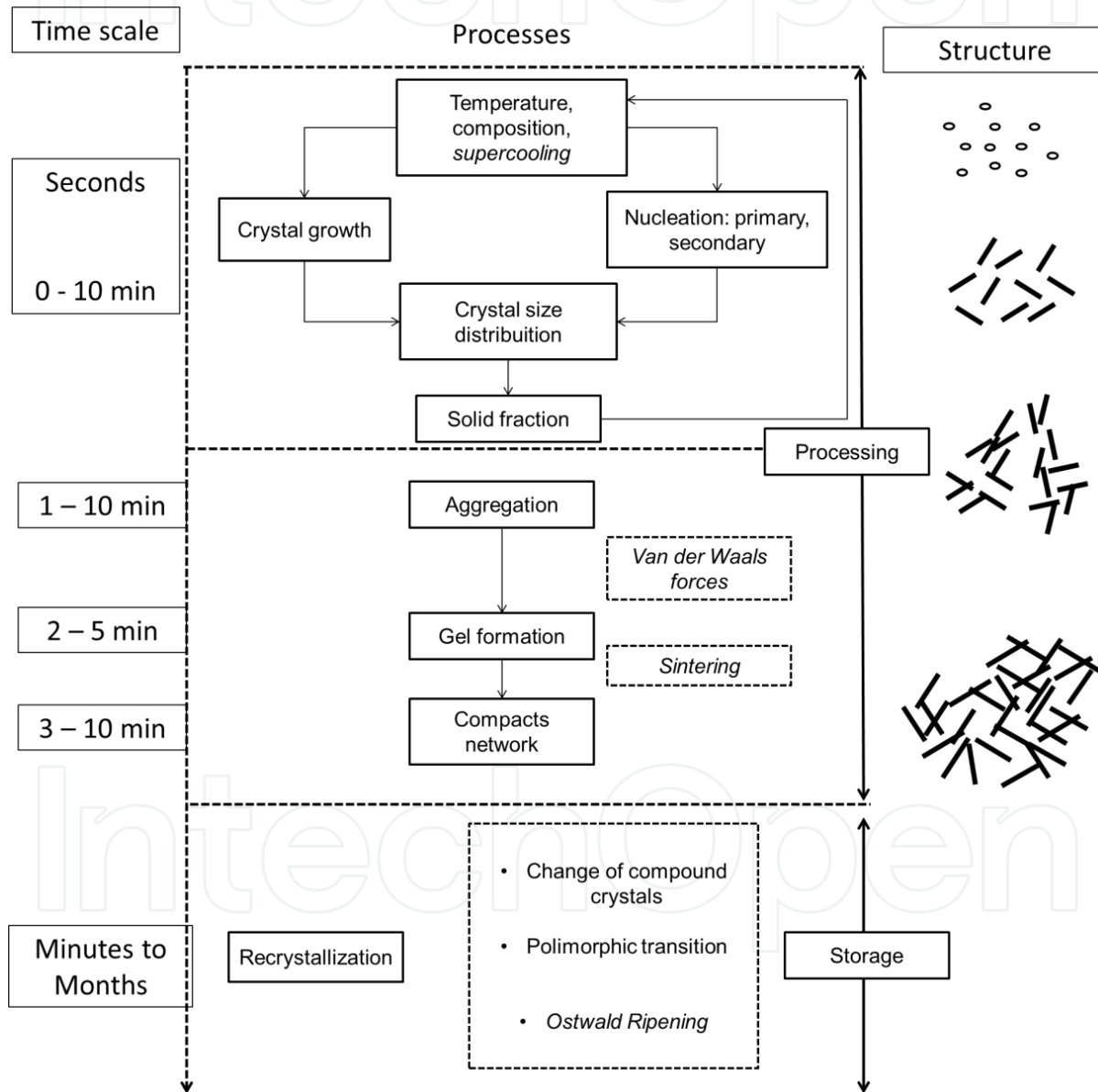

Figure 2. Process schematic of the process involving crystallization and storage of fats. Adapted from [55].

Crystallization of fats is a critical factor associated with the structure and properties of most foods. The stability of many processed food products is influenced by changes in the physical

state of the fats and changes in the crystallization processes, since the events of nucleation and crystal growth occur simultaneously at different rates as they are affected by conditions such as degree and rate of super-cooling, viscosity and agitation [13].

In the initial stages of food processing, the relative rates of nucleation and crystal growth determine the distribution, shape and size of the crystals, parameters that are directly related to the characteristics of consistency and texture. However, during the storage phase, several post-crystallization phenomena may occur, significantly affecting the properties and stability of foods. These include polymorphic transitions to thermodynamically more stable phases, formation of new crystals and crystal growth, and migration of oil or small crystals. It should be noted, however, that such events are not chronological; polymorphic transitions can occur even in the early stages of processing [31].

Additionally, in post-crystallization processes the phenomena known as sintering or bonding of adjacent surfaces can be verified, as well as spontaneous dissolution, also known as Ostwald ripening. The term sintering is described as the formation of solid bridges between fat crystals, with formation of a cohesive network associated with the undesirable increase in the hardness of the fat phase. Ostwald ripening, in turn, is associated with dissolution of previously existing small crystals in the fat phase and development of crystals with undesirable dimensions and weak crystal lattices, which causes loss of consistency of the products [56].

Furthermore, in some specific products the control of crystallization means, above all, avoiding this process, even if it is thermodynamically favored or due to storage or processing conditions [8]. Thus, control of crystallization and polymorphic transitions in fats is a factor of fundamental importance for the food industry.

5. Fats for industrial use

5.1. Interesterified fats

Interesterification is a technological alternative to the partial hydrogenation process, since it enables the production of oils and fats with specific functionalities. Due to the growing concern of the nutritional impact of *trans* fatty acids on health, interesterification has been indicated as the main method for obtaining plastic fats with low levels of *trans* isomers or absence of these compounds. In contrast to hydrogenation, this process does not promote the isomerization of double bonds of fatty acids and does not affect the their degree of saturation [57].

In the interesterification process the fatty acids are rearranged in the glycerol molecule. Interesterification is promoted by an alkaline catalyst (chemical interesterification) or by lipases (enzymatic interesterification). The alkaline catalysts most frequently used are sodium methoxide and sodium ethylate [58]. In chemical interesterification the fatty acids are randomly distributed in the glycerol molecule along the three available positions within each molecule. When specific lipases are used to catalyze the interesterification reaction, rearrangement can occur in the *sn1* and *sn3* positions of the glycerol molecule, maintaining the *sn2* position [59].

Chemical interesterification is currently the process most utilized by industry. The random distribution of fatty acids along the glycerol molecules leads to changes in the triacylglycerol composition, which alters the overall solids profile of the fat. In interesterified fats, the random distribution of fatty acids results in great variability of TAGs, with intermediate melting points (S_2U and U_2S). Such variability in TAGs, associated with the formation of partial acylglycerols, promotes slower crystallization and indefinite maintenance of the polymorphic form β' [58, 60, 61]. Other observations, such as decreased size of the crystals as well as distribution in the crystal lattice, were also observed in some studies [62].

5.2. Palm oil

Palm oil is obtained from the mesocarp of the fruit *Elaesis guineensis*. It is semi-solid at room temperature, consisting primarily of TAGs of palmitic and oleic acids. Palm oil is the vegetable oil most used worldwide in the food industry. In June 2013, world production of palm oil reached 58 million tons, surpassing the production of soybean oil [63]. As a result of increased production, many studies are focused on palm oil, especially regarding its crystallization behavior and nutritional aspects. Compared to other vegetable oils, palm oil presents a unique and differentiated fatty acid composition, containing similar percentages of saturated and unsaturated fatty acids. It also presents a significant content of saturated fatty acids (10 to 16%) in the *sn-2* position of the TAGs, as well as significant levels of palmitic acid (44%). In addition to these features, palm oil contains small percentages of MAGs and DAGs as minor components, which are produced during maturation of palm fruits and oil processing. The DAGs, specifically, correspond to 4-8% of the composition of palm oil, with variations according to origin and processing conditions. The removal of these compounds, however, is difficult even under optimal refining conditions [18, 64, 65].

The crystallization behavior of palm oil is extremely important from a commercial point of view, because it is characterized by the crystal habit β', a fact that, combined with its characteristics of plasticity, ensures its application in margarines, spreads, bakery and confectionery fats, as well as general purpose shortenings. The functional properties of palm oil and its fractions appear to be strongly related to its composition and the quantity and type of crystals formed at the temperature of application. However, the crystals of palm oil require a long time for $\alpha \rightarrow \beta'$ transition, a factor considered inadequate from an industrial process standpoint. Resistance to transformation into β' is mainly attributed to the DAGs. Recent studies on the interactions between TAGs and DAGs in palm oil during crystallization show that the latter have a deleterious effect on the characteristics of crystallization, with intensity proportional to the concentration of these minority lipids in palm oil and its fractions [66, 67]. According in [68], the negative effect of DAGs on the crystallization of palm oil may be related to the low nucleation rate of TAGs in the presence of these compounds.

In addition to the slow crystallization of palm oil, another factor of great concern in industry is its post-processing stability. Palm oil is often associated with hardening problems during storage. In some products based on this raw material, undesired crystal growth occurs which results in gritty texture and poor spreadability [69]. These crystalline shapes may reach dimensions greater than 50 μm after a few weeks of storage, leading to non-uniformity of the

processed products [68]. In margarines, specifically, the formation of crystal agglomerates with mean diameter between 0.1 and 3mm is observed, which can easily be observed with the naked eye [70]. In [71] found that the main TAGs of palm oil, 1-palmityl-2-oleoyl-palmitine (POP) and 1-palmityl-diolein (POO), have limited miscibility with each other, which results in formation of large POP crystals surrounded by POO. When these agglomerates are formed, there occurs the joining of other saturated TAGs in a process that promotes $\beta' \rightarrow \beta$ transition. Therefore, to ensure the stability of the β' polymorph in palm oil-based products this is a question of great industrial interest, given the great economic importance associated with the use of this raw material.

5.3. Palm Mid Fraction (PMF)

The product of the first fractionation stage of palm olein is termed the soft palm mid fraction (soft PMF), which presents high levels of monounsaturated triacylglycerols, rapid melting and tendency to crystallize in β', making it an excellent raw material for the production of margarines and shortenings in general [72, 73].

Classically, two methods are proposed for the production of soft PMF: the olein route (most common in Asia) and the stearin route, which is preferentially used in South America because of the need for olein with high iodine index in the first fractionation stage. The best CBE's are obtained via the olein route, where the second fractionation stage of the triacylglycerols SSU-SUS focuses selectively on soft PMF. In dry fractionation, soft PMF concentrates more than 73% of SSU-SUS triacylglycerols, and the content of SSS triacylglycerols is low. Thus, refractionation of soft PMF produces an excellent hard PMF, particularly enriched in SSU-SUS triglycerides (85%-90%) with low content of SSS triglycerides, and the DAG content can be kept low enough to avoid any adverse effect on the crystallization properties of the fraction [74].

Due to the closely related structural properties, TAGs can produce co-crystals by intersolubility, which frequently present solid solutions, monotectic interactions, eutectic systems and formation of molecular compounds [1]. As a result, the efficiency of fractionation depends not only on the separation efficiency, but is limited by the phase behavior of TAGs in the solid state. Thus, intersolubility of TAGs is a challenge in the dry fractionation process, including the route: olein $\rightarrow$ soft PMF $\rightarrow$ hard PMF.

6. Crystallization problems in raw materials of great industrial importance

Most natural oils and fats have limited application in their unaltered forms, imposed by their particular composition of fatty acids and TAGs. Thus, oils and fats for various industrial applications are chemically modified by hydrogenation or interesterification, or physically by fractionation or mixture [75]. Although used for a long time, partial hydrogenation results in significant formation of *trans* fatty acids, associated with negative health effects [76].

In Brazil, controversial issues surrounding the role of *trans* fatty acids in the diet have led to progressive changes in legislation, aiming to include more information for consumers.

Resolution RDC No. 360, of December 23, 2003, approved by the MERCOSUR, obligated the declaration of *trans* fatty acids on the nutritional label of foods. Companies had until July 31, 2006 to meet regulations, so that the *trans* fat content is declared in relation to the standard portion of a certain food, together with statements of total and saturated fats [77]. In response, Brazilian industries opted for the progressive substitution of *trans* fat in many products through the development of base fats with functionality and economic viability equivalent to partially hydrogenated fats, but without substantial increase in the content of saturated fatty acids in foods.

In this sense, interesterification was found to be the main alternative for obtaining plastic fats with low levels of *trans* isomers or lack thereof. In particular, chemical interesterification of liquid oils with fully hydrogenated oils (hardfats) is currently the alternative of greatest versatility to produce zero *trans* fats, producing base fats favorable for the preparation of commonly used shortenings [61]. The use of blends, i.e., mixtures of fats with different physical properties, and fractionation also represent additional alternatives to obtain base fats with appropriate physical and plasticity properties to be used in various products, although with potential limited by the chemical composition of the raw materials [21].

Although the interesterification, fractionation and mixing processes are very functional from a technological point of view, the substitution of partially hydrogenated fats in food products, especially in shortenings and confectionery products, is currently a challenge since appropriate crystallization and texture properties are difficult to obtain in the absence of *trans* fatty acids [78].

In particular, adequacy of crystallization kinetics of these base fats is of utmost importance so that their use may be adjusted to the limitations of industrial processes and to improve control of processing steps that involve recrystallization of the fat fraction, ensuring quality of the final product [79]. Contrarily, previously standardized processing times and equipment must be altered according to the characteristics of the fat used. This fact becomes particularly important as new fat fractions began to replace partially hydrogenated fats in most industrial applications, mainly in the production of biscuits and bakery products, where it is noted that fats with the same apparent solids profile present very different crystallization properties [80]. In the specific case of interesterified fats, the formation of partial acylglycerols, such as MAGs and DAGs as a result of chemical interesterification, can influence the crystallization kinetics via alterations to the crystal nucleation process [81]. According in [82], 0.1% of the catalyst sodium methoxide, used for randomization, can produce between 1.2 and 2.4% of MAGs+DAGs. Because the typical catalyst content used industrially ranges from 0.1 to 0.4%, concentrations of these minority lipids may be greater than 9%. Although minority lipids present influence on the crystallization properties of these fats, their complete removal is still difficult and expensive, especially on a large scale [22].

Considering that in the Brazilian industry this substitution process is relatively recent, the problems of crystallization behavior due to the unsuitability of new fat fractions are numerous and aggravated, mainly due to regional differences in climate and conditions of transport and storage. In this context, highlighted problems include unwanted polymorphic transitions, oil exudation, development of fat bloom, formation of crystalline agglomerates, and base fats with

a maximum solid fat content or induction periods incompatible with certain industrial applications. Studies on modification, stabilization and control of crystallization of these base fats are therefore of crucial importance for development of the edible oils industry.

7. General characteristics of emulsifiers

In a classic definition, an emulsifier is an expression applied to molecules which migrate to interfaces between two physical phases, and are therefore more concentrated in the interfacial region than in the solution phase [83]. The main molecular characteristic of an emulsifier is its amphiphilic nature, characterized by an ionic group (polar region) and a hydrocarbon chain (nonpolar region). According to their polar and nonpolar regions, emulsifiers are designated as hydrophilic or lipophilic, which affects their solubility in water or oil [84]. Thus, the term hydrophilic-lipophilic balance (HLB) was suggested, which measures the affinity of an emulsifier for oil or water. Regarding emulsifiers in foods, lipophilic properties are generally the most important, but the hydrophilic-lipophilic balance (HLB) may vary considerably according to the chemical composition of the emulsifier. The dual affinity of emulsifiers results in the formation of a single phase between initially immiscible substances (emulsion). Furthermore, these compounds perform functions that in some products are not related to emulsification, including modification of the crystal habit during crystallization of oils and fats [83].

The concept of HLB makes it possible to characterize the various emulsifiers or mixtures of emulsifiers. In general, the following guidelines are used for applying an emulsifier based on its HLB:

- HLB of 3-6: a good water/oil emulsifier;

- HLB of 7-9: a good wetting agent;

- HLB of 10-18: a good oil/water emulsifier.

Nevertheless, the HLB value is limited because it provides a one-dimensional description of the emulsifier properties, and omits information such as the molecular weight and temperature dependence. It is also difficult to calculate useful HLB values for various important emulsifiers in food applications (eg: phospholipids). Additionally, HLB values do not include the important crystallization properties of emulsifiers [85].

Regarding the crystallization properties, in the crystal structure of emulsifiers, the predominant factor is the hydrophilic portion which is the relatively larger portion of the molecule. The size of the hydrophilic group, along with the extension and spatial distribution of hydrogen bonding between adjacent groups, has a much larger influence on the molecular packing of the crystal than the nature of the fatty acid chain. A simple emulsifier, such as a monoacylglycerol, generally crystallizes in the double chain length (DCL), while those with larger hydrophilic groups more frequently crystallize in the SCL configuration (Figure 3) [83].
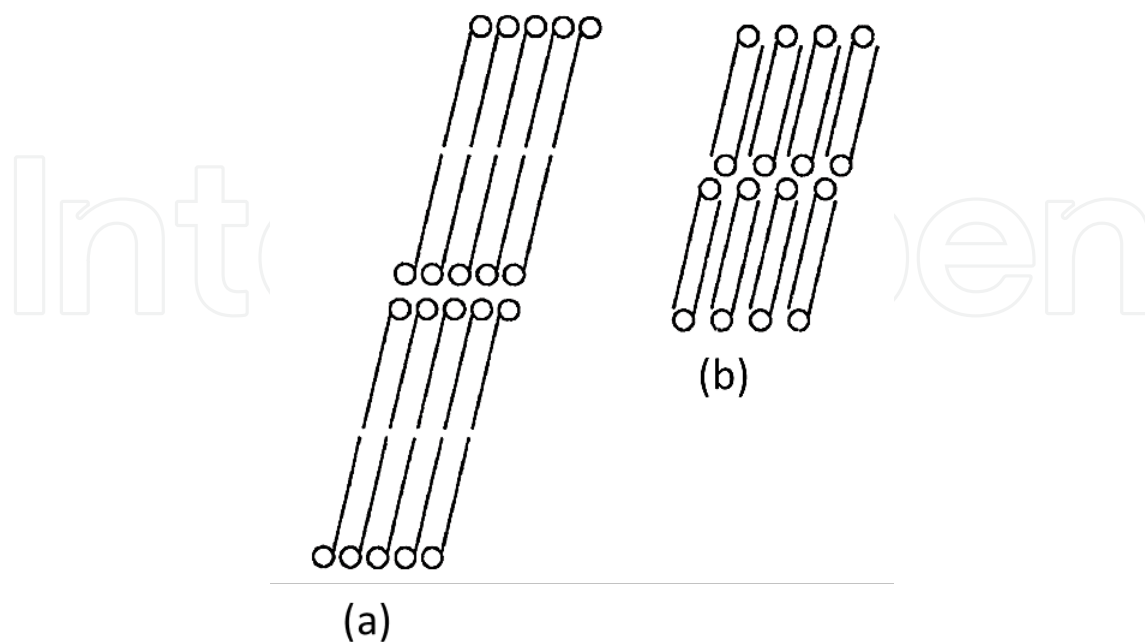
Figure 3. Configurations in (a) DCL (*double chain length*) and (b) SCL (*single chain length*) (STAUFFER, 1999)

Among crystallization properties, an important feature of emulsifiers is their ability to create mesophases. Mixtures of emulsifiers with water form different physical structures, depending on the emulsifier/water ratio and temperature. These mixtures are opalescent dispersions, often called "liquid crystals", but are better known as mesophases. This term (which means "between stages") reflects the nature of the mixture. On a micromolecular level, the emulsifier agent and water are separated phases, but at the macro level the mixture becomes uniform and is stable (that is, the phases do not separate) [86]. Liquid crystals are thermodynamic mesophases of the condensed material with a certain degree of ordering between the crystalline solid and liquid states [87]. There are two main families of liquid crystals: thermotropic and lyotropic. Thermotropic liquid crystals are composed of molecules, or mixture of molecules, which exhibit shape anisotropy (also known as anisometry). These molecules may have the shape of rods (most common), disks and arcs, among others. The structural and ordering differences of these individual molecules occur as a function of temperature, and therefore are called thermotropic. On the other hand, lyotropic liquid crystals are mixtures of amphiphilic molecules and polar solvents, which under determined conditions of temperature, pressure and relative concentrations of different components, present the formation of aggregated molecular superstructures, which are organized in space, showing some degree of order [88]. The amphiphilic molecules such as emulsifiers may present both behaviors (thermotropic and lyotropic) in this case, called amphotropic liquid crystals [88, 89]. A simplified schematic of the formation of some thermotropic and lyotropic mesophase structures is shown in Figure 4.
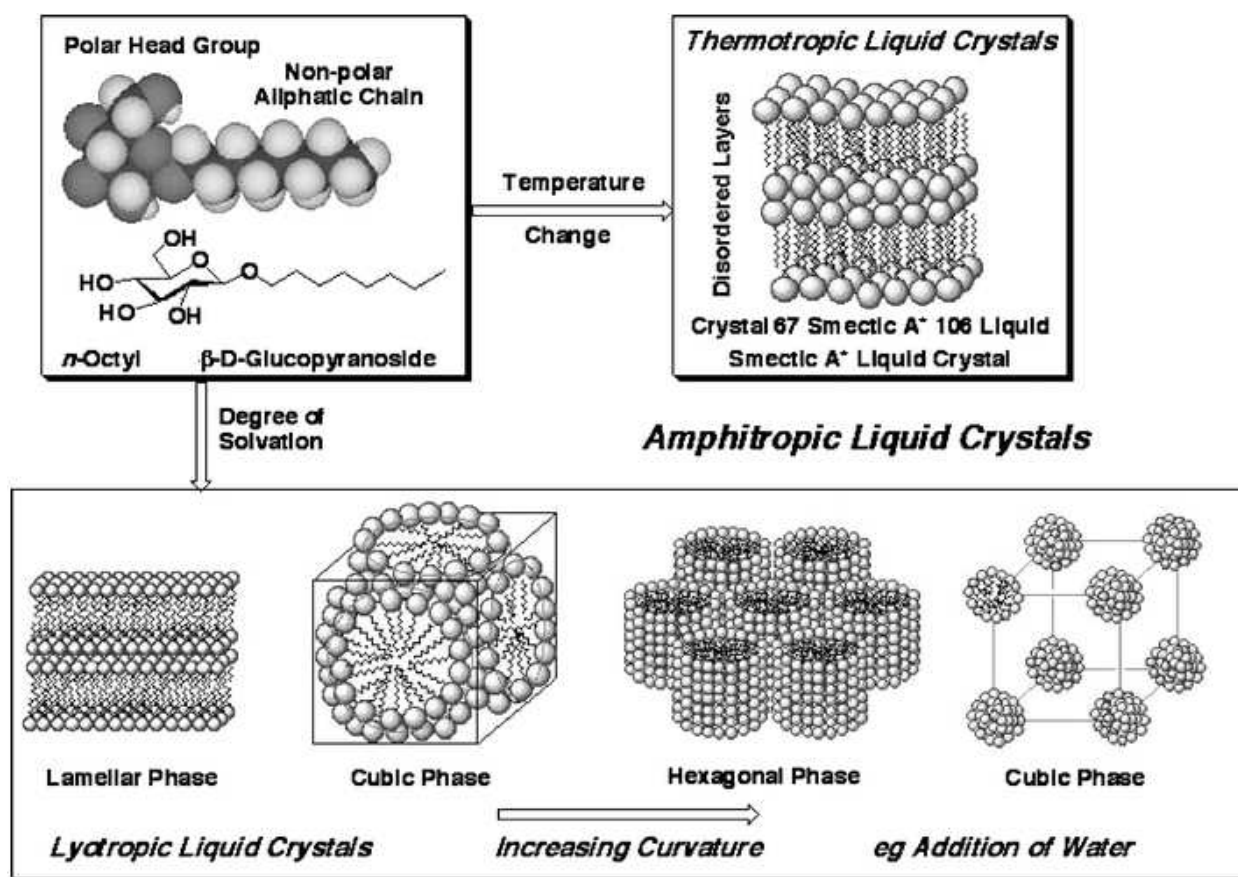
Figure 4. Structural schematic of the thermotropic and lyotropic mesophases formed by n-octyl β-D-glucopyranoside. Adapted from [89].

7.1. Use of emulsifiers as crystallization modifiers

In addition to their known functions of emulsification and stabilization of emulsions, emulsifiers can modify the behavior of the continuous phase of a food product, giving it specific benefits. In fat-rich products, emulsifiers may be used to control or modify the crystallization properties of the fat phase. Study of the effects of emulsifiers in fat systems is of great interest to improve industrial products, particularly with respect to fat for use in chocolate, confectionery and baking. However, the role of these compounds as modifiers of crystallization in natural and commercial fats is little exploited in technical literature [17]. To date, the vast majority of studies on the use of emulsifiers as modifiers of the crystallization process in fats were carried out with fully hydrogenated oils, model systems or pure TAGs, and therefore do not reflect the need to control crystallization in fats for industrial application [9, 90].

In general, the effect of emulsifiers appears to be related to different crystalline organizations and the creation of imperfections. Some of them can slow transformations via steric hindrance, while others promote these transformations by favoring molecular displacements [3]. Two different mechanisms have been reported in literature to interpret the effect of emulsifiers on crystallization of fats. The first refers to the action of these additives as hetero-nuclei, acceler-

ating crystallization by direct catalytic action as impurities. During crystal growth, emulsifiers would be adsorbed at the surface of the crystals and would therefore modify the incorporation rate of TAGs and crystal morphology. The second mechanism, of greater consensus among various authors, considers that the TAGs and emulsifiers would be amenable to co-crystallize due to the similarity between their chemical structures. Thus, the structural dissimilarity also entails delays in nucleation and potential inhibition of crystal growth [7, 86].

According to this second mechanism, emulsifiers are associated with triacylglycerol molecules by their hydrophobic groups, especially through acyl-acyl interactions. The acyl group of emulsifiers determines its functionality with respect to the TAGs. The main effects of these additives on the crystallization of fats occur during the stages of nucleation, polymorphic transition and crystal growth, altering physical properties such as crystal size, solid fat content and microstructure. The question of promoting or inhibiting crystallization, however, is still debatable. In general, studies indicate that emulsifiers with acyl groups similar to the fat to be crystallized accelerate this process [12].

Currently, it is known that the behavior of emulsifiers during the crystallization of fats can be divided into three cases: (1) limited miscibility between emulsifier molecules and TAGs: in this situation the emulsifier acts as an impurity and the interaction results in imperfect crystals, which may promote or retard crystal growth and polymorphic transitions, depending on the compatibility of hydrophobic ends in their structures; (2) high degree of miscibility between emulsifiers and TAGs that promotes the formation of molecular compounds; (3) total immiscibility between emulsifiers and TAGs, where emulsifiers can act as crystallization germs and microstructure modifiers [11, 86].

Emulsifiers with high potential for controlling crystallization of base fats include sorbitan esters of fatty acids, fatty esters and polyesters of sucrose, commercial standard lecithin and chemically modified lecithin, and the polyglycerol polyricinoleate [30]. Many studies have confirmed that emulsifier affect the crystallization induction times, the composition of nucleation germs, rates of crystal growth and polymorphic transitions [91]. However, the results are still very incipient, and require greater explanation.

7.2. Sugar-based emulsifiers

While the derivatization of oils and fats to produce a variety of emulsifiers with a wide range of application has shown to be well established for many years [92], the industrial production of emulsifiers based on oils, fats and carbohydrates is relatively new. Such emulsifiers result from a product concept based on the exclusive use of renewable resources, where sucrose, glucose and sorbitol are the most used raw materials in industry. The sugar-based emulsifiers most used in the food industry are sorbitan and sucrose esters.

7.2.1. Sorbitan esters

Sorbitol is a hexameric alcohol, obtained by the hydrogenation of glucose. Its free hydroxyl groups can react with fatty acids to form sorbitan esters (SE). In SE production, a reaction mixture containing a specific fatty acid, sorbitol and the catalyst (sodium or zinc stearate) is

heated in an inert atmosphere to promote simultaneous esterification and cyclization reactions. The fatty acid/sorbitol mole ratio determines the formation of monoesters and triesters. The SE most well-known and used industrially include lauric, palmitic, stearic and oleic acids [17]. Figure 5 shows the chemical structure of a sorbitan tristearate.

Sorbitan tristearate (STS or *Span* 65) and sorbitan monostearate (SMS) are recognized for their ability to efficiently modify crystal morphology and consistency of fats, such as anti-bloom agents in confectionery products containing cocoa butter and in substitutes of cocoa butter, indicated as potential controllers of crystallization. It is assumed that these compounds can delay or inhibit the transition of fat crystals to a more stable form. Moreover, the SE showed to be particularly effective in stabilizing the polymorph β' in margarines and modification of the solid fat content of fats in general, promoting fusion profiles adequate for the body temperature [18]. They can also be selective as dynamic controllers of polymorphic transitions in fat, due to their ability to create hydrogen bonds with neighboring TAGs, in a process known as The Button Syndrome, whereby the presence of a specific emulsifier does not form a preferred polymorph, but rather controls the degree of mobility of the molecules and their potential to undergo configurational changes. In this process, emulsifiers can modulate the polymorphic transformations in the solid state or via the liquid state, and the temperature regime used to control the physical state of crystals during the polymorphic transition and extension of the mobility of the molecules, thereby regulating the rate of polymorphic transformation [4].
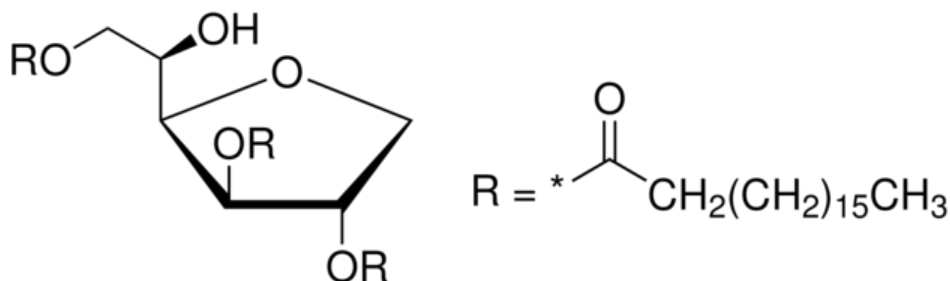

Figure 5. Chemical structure of Sorbitan Tristearate (STS).

According in [91], STS is the additive with greatest potential for modification of crystallization in cocoa butter, particularly in inhibiting the βV → β VI transition and fat bloom due to its high melting point (55°C) and chemical structure similar to the TAGs present in the oils and fats, permitting facilitated co-crystallization by this emulsifier and formation of solid solutions with these TAGs. In [93], the addition of 0.5% (w/w) of STS to base fats for margin had a stabilizing effect on the polymorph β'. According in [11] observed the formation of small crystal aggregates in mixtures of palm oil/palm kernel olein when adding 0.09% (w/w) of STS, in addition to increasing the rate of crystallization of these mixtures. In a review article, in [16] emphasized the use of STS and/or combinations thereof with other emulsifiers such as soy lecithin, the current alternative of greatest interest for the control of polymorphic transitions and structuring of the crystal lattice in fats, since the TAGs-STS interaction promotes the formation of

regular crystals that melt at 40°C, the melting point characteristic of most base fats for industrial applications.

7.2.2. Sucrose esters

Sucrose fatty esters can be used in a wide range of food applications and are mainly utilized in the bakery, confectionery, desserts and special emulsion industries [94]. Sucrose esters, particularly mono-and di-esters, are extremely functional emulsifiers, since they provide a number of unique advantages for the food industry. They are non-toxic compounds, without taste or odor, easily digested sucrose and fatty acids, as well as biodegradable under aerobic and anaerobic conditions. They are produced by interesterification of sucrose and fatty acids by various reaction types and conditions. Their structure is typically composed of polar and nonpolar groups in the same molecule as other emulsifiers, but the eight possible positions for esterification with fatty acids allow for these molecules to obtain different lipophilic/hydrophilic properties. Partially esterified sucrose esters, especially the mono-, di-and tri-esters, are more versatile for use in food applications, where the degree of esterification is controlled by the fatty acids/sucrose ratio in the reaction mixture. Monoesters (~70% of monoesters) are hydrophilic, while the di-, tri-, and polyesters are increasingly hydrophobic [95]. The degree of saturation and size of fatty acid chains used also significantly influences the properties of these compounds [17, 86]. Figure 6 shows the chemical structure of a sucrose ester of stearic acid and that of behenicacid.
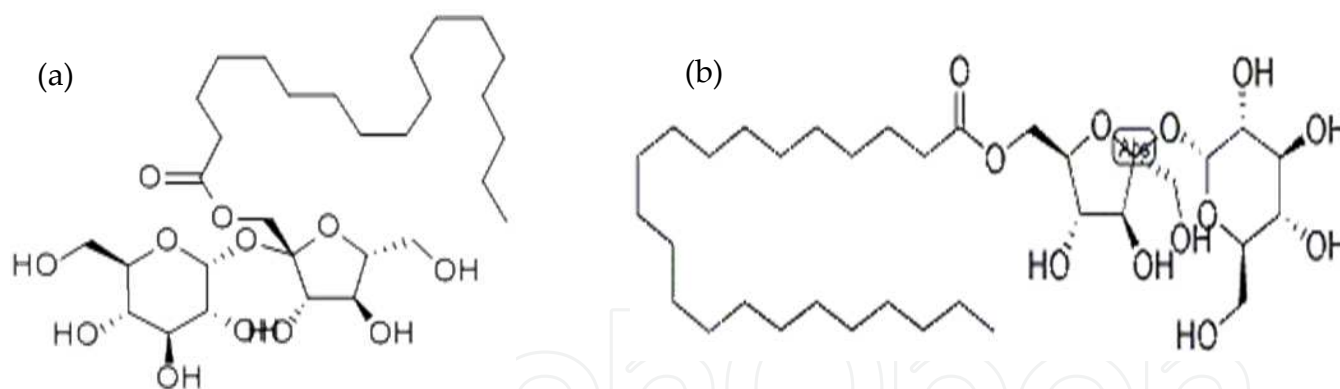

Figure 6. Chemical structures of: (a) sucrose stearate and (b) sucrose behenate.

The fatty acids most commonly used in sucrose esters are the lauric (C12), myristic (C14), palmitic (C16), stearic (C18), oleic (C18) and behenic acids (C22). By changing the nature or number of fatty acid groups, a wide range of HLB values can be obtained. Commercial sucrose esters are mixtures with various degrees of esterification, due to their complexity, and exhibit diverse behaviors, like lipids. Consequently, they are used in studies on the crystallization of fats. The sucrose esters most studied to date are esters of stearic acid and palmitic acid, especially in the studies of [9, 96, 97]. However, according to [9], few studies explore the effect of these emulsifiers on the induction period, and the rate of crystallization and development of polymorphic forms in fatty systems.

Acknowledgements

Author details

Maria Aliciane Fontenele Domingues[1*], Ana Paula Badan Ribeiro[1], Theo Guenter Kieckbusch[2], Luiz Antonio Gioielli[3], Renato Grimaldi[1], Lisandro Pavie Cardoso[4] and Lireny Aparecida Guaraldo Gonçalves[1]

*Address all correspondence to: aliciane@fea.unicamp.br

1 School of Food Engineering, University of Campinas, Campinas, Brazil

2 School of Chemical Engineering, University of Campinas, Campinas, Brazil

3 Faculty of Pharmaceutical Sciences, University of São Paulo, São Paulo, Brazil

4 Institute of Physics "Gleb Wataghin", University of Campinas, Campinas, Brazil

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