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REVIEW

Crystallization modifiers in lipid systems

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Abstract Crystallization of fats is a determinant physical event affecting the structure and properties of fat-based products. The stability of these processed foods is regulated by changes in the physical state of fats and alterations in their crystallization behavior. Problems like polymorphic transitions, oil migration, fat bloom development, slow crystallization and formation of crystalline aggregates stand out. The change of the crystallization behavior of lipid systems has been a strategic issue for the processing of foods, aiming at taylor made products, reducing costs, improving quality, and increasing the applicability and stability of different industrial fats. In this connection, advances in understanding the complex mechanisms that govern fat crystallization led to the development of strategies in order to modulate the conventional processes of fat structuration, based on the use of crystallization modifiers. Different components have been evaluated, such as specific triacyglycerols, partial glycerides (monoacylglycerols and diacylglycerols), free fatty acids, phospholipids and emulsifiers. The knowledge and expertise on the influence of these specific additives or minor lipids on the crystallization behavior of fat systems represents a focus of current interest for the industrial processing of oils and fats. This article presents a comprehensive review on the use of crystallization modifiers in lipid systems, especially for palm oil, cocoa butter and general purpose fats, highlighting: i) the removal, addition or fractionation of minor lipids in fat bases; ii) the use of nucleating agents to modify the crystallization process; iii) control of crystallization in lipid bases by using emulsifiers. The addition of these components into lipid systems is discussed in relation to the phenomena of nucleation, crystal growth, morphology, thermal behavior and polymorphism, with the intention of providing the reader with a complete panorama of the associated mechanisms with crystallization of fats and oils.

Keywords Oils · Fats · Crystallization · Industrial processing · Minor lipids · Nucleating agents · Emulsifiers

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Introduction

Oils and fats

Lipids are represented by fatty acids and their derivatives, or functionally and biosynthetically substances related with these compounds. Edible oils and fats are essential nutrients in the human diet, having a vital role for providing essential fatty acids and energy (Scrimgeour 2005).

Chemically, oils and fats are multi-component mixtures composed predominantly of triacylglycerols (TAGs), which are esters of glycerol and fatty acids. TAGs consist of a glycerol moiety with each hydroxyl group esterified to a fatty acid. In nature, they are synthesised by enzyme systems, which determine that a centre of asymmetry is created about carbon-2 of the glycerol backbone, so they exist in enantiomeric forms, with different fatty acids in each position (*sn-1*, *sn-2* or *sn-3*), according to Fig. 1. Additional components include polar (or minor) lipids, such as diacylglycerols (DAGs), monoacylglycerols (MAGs), free fatty acids,

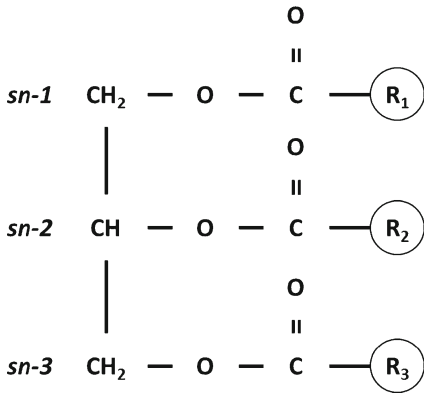

Fig. 1 Triacylglycerol molecule. R1, R2 and R3 represent alkyl chain

phospholipids, glycolipids and sterols (Nichols and Sanderson 2003).

The physical behavior of lipids depends on the characteristics of the alkyl chain of the fatty acids: saturated or unsaturated fatty acids, *cis* or *trans* configuration and chain size. The melting point increases with chain length and decreases with increased unsaturation. Among saturated acids, odd chain acids are lower melting than adjacent even chain acids. The presence of cis-double bonds markedly lowers the melting point, the bent chains packing less well. *Trans* fatty acids have melting points much closer to those of the corresponding saturates (Scrimgeour 2005).

Particularly, the triacylglycerol composition determines the physical properties of the oils and fats, affecting the structure, stability, flavor and the sensory and visual characteristics of foods. The oils are liquid at room temperature and the fats are apparently solid, all formed of a complex mixture of TAGs (O'Brien 2008).

Crystallization of lipids

Plastic fats are a crystalline network on a continuous oil matrix (Sato 2001). The crystallization process is the system arrangement as a result of a driven force, characterized by total or partial restriction of movement caused from the physical or chemical bonds between the TAGs molecules. Differences in crystalline forms result from different molecular packing. Therefore, crystals consist of molecules arranged in fixed patterns known as reticulates. Their high degree of molecular complexity allows a same set of TAGs to be packed in several different structures that are relatively stable (Foubert 2007).

Crystallization of lipids has important implications in the industrial food processing, since these products have physical characteristics that largely depend on fat crystals. Such products include chocolates, margarines, spreads, fats for bakery and confectionery, dairy products and general-purpose shortenings (Sato 2001).

Crystallization of fats provides some important properties of processed foods: consistency and plasticity of rich fat products, such as butter, margarine and chocolate, during the stages of production and storage; sensorial properties, such as melting sensation in the mouth; physical stability related to the formation and growth of crystals, oil migration and coalescence of particles and emulsions; and appearance, such as the brightness in chocolates (Foubert et al. 2007). Crystallization of TAGs is generally considered the most important event in fat structuring, although the crystallization of minor lipids, such as DAGs, MAGs and phospholipids, represents a fundamental role in the quality of various products (Metin and Hartel 2005).

Mechanism of crystallization of lipids

The process of crystallization includes the nucleation and crystal growth. Nucleation involves the formation of aggregates of molecules that have exceeded a critical size and are therefore stable. Once a crystal nucleus has formed, it begins to grow by incorporating other molecules from the adjacent liquid layer, which is continuously filled by the supersaturated liquid that is around the crystal (Boistelle 1988).

A nucleus is the smallest crystal that can exist in a solution in a certain temperature. The formation of a nucleus from the liquid phase, or the nucleation process, requires the organization of molecules in a crystalline lattice of critical size, from overcoming an energy barrier. Nucleation mechanisms are generally classified as primary nucleation, which can be homogeneous or heterogeneous, and secondary nucleation. Homogeneous nucleation occurs from the junction of isolated molecular species, which form dimers, trimers and subsequently continue the accumulation process up to when a possible nucleus can be formed depending on the temperature and supersaturation conditions. This kind of nucleation, however, rarely occurs under the conditions of industrial processes. In practice, the nucleation of most systems is usually dominated by the heterogeneous mechanism, in which external catalytic sites or surfaces, such as molecules of differentiated composition, serve 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 to form the nucleus. The secondary nucleation is the formation of a new nucleus in the presence of existing crystals, which may occur if microscopic crystalline elements are separated from a crystalline surface already formed, therefore resulting in the fracture of crystals in small stable nuclei (Metin and Hartel 2005; Lawler and Dimick 2002).

When the nuclei formed reach favorable dimensions, these elements become crystallites, whose growth depends not only on external factors (supersaturation, solvents, temperature,

impurities), but also on internal factors (structure, links, defects). Therefore, the crystal growth rate can vary by several orders of magnitude. The growth occurs by the binding of molecules to a crystalline surface. At the same time in which molecules are bound to the surface of a crystal, some molecules are also deactivated. There is a continuous movement of molecules on the surface of the crystal, and the result of these processes determines the growth rate, which is directly proportional to the subcooling and varies inversely with the viscosity system (Foubert et al. 2007). Although nucleation and crystal growth are often considered as distinct events, they are not mutually exclusive. Nucleation also occurs while the crystals grow from the molecular clusters formed by the breaking of other existing crystals (Wright et al. 2000a, b).

Crystallization kinetics

The crystallization kinetics intensively influences the final structure of fats and is intrinsically linked to their rheological and plasticity properties. By monitoring the formation of crystalline solid material as a function of time, the nature of the process of crystallization can be determined (Foubert 2007).

The characterization of the crystallization kinetics can be done according to the induction period (τ_{SFC}) or nucleation period (relative to the beginning of crystal formation) and maximum solid content - SFC_{max}. Induction time reflects the time required for a stable nucleus of critical size to be formed in the liquid phase (Himawan et al. 2006). As a definition, τ_{SFC} is the time required to obtain a crystal nucleus per volume. The τ_{SFC} generally increases with increasing isothermal crystallization temperature and with decreasing melting point of the sample. Another useful parameter for the evaluation of isothermal crystallization is the crystallization stabilization time (t_{ec}), defined as the total time for the stabilization of the solid fat content at a given temperature. This parameter is the sum of the characteristic times for nucleation and crystal growth (Hachiya et al. 1989).

The most widely used model for the description of the isothermal phase transformation kinetics is the Avrami model, developed in 1940, which relates the kinetic experimentally determined with the growth form and final structure of the crystalline network (Narine et al. 2006). The Avrami equation gives an indication of the nature of the growth process of crystals:

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

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 consideration both the nucleation and crystal growth rate; and n is the Avrami exponent, which indicates the crystal growth mechanism (Wright et al. 2000a, b). From the effects of the combination of k and n, we can calculate the crystallization half time ($t_{½}$), which reflects the magnitude of the Avrami constant, being defined as the time required to achieve 50 % of the crystals (Saberi et al. 2011).

$$t_{§} = (0.693/k)^{1/n}$$

Currently, the most common analytical technique to investigate the crystallization kinetics of fats is the nuclear magnetic resonance (NMR). However, several analytical techniques such as differential scanning calorimetry (DSC), polarized light microscopy (PLM), as well as the rheological and turbidimetric techniques can be employed successfully. The understanding of the phenomena involved in the crystallization kinetics is better achieved with the combined use of several instrumental methods (Cerdeira et al. 2004).

Polymorphism

Long-chain compounds, such as fatty acids and their esters, can exist in different crystalline forms. Solids with the same composition that can exist in more than one crystalline form are called polymorphs. Polymorphism can be defined in terms of the ability to manifest different unit cell structures as a result of various molecular packings. The crystal habit is defined as the crystal form. From a crystallographic perspective, the habit reflects the direction of the growth within the crystal, while the morphology describes the set of faces determined through the symmetric elements of the crystal. This distinction allows crystals of the same morphology to have different crystalline habits (Lawler and Dimick 2002).

In a fat, crystals are solids with atoms arranged in a regular three-dimensional pattern. A cell is the repeating unit that makes up the integral structure of a given crystal. A sub-cell, in turn, is the smallest periodic structure that exists in the actual cell unit, being defined as the transverse mode of packing of the aliphatic chains in TAGs. The polymorphic forms of a fat are identified based on their sub-cell structure (Boistelle 1988). In lipids, three specific types of sub-cells are predominant, the polymorphs α, β' and β, according to the current polymorphic nomenclature (Fig. 2). Form α is metastable, with hexagonal chain packing. Form β' has intermediate stability and orthorhombic perpendicular packing, while form β has greater stability and triclinic parallel packing. The melting temperature increases with increased stability ($\alpha \rightarrow \beta' \rightarrow \beta$), as a result of differences in density of the molecular packing (Martini et al. 2006).

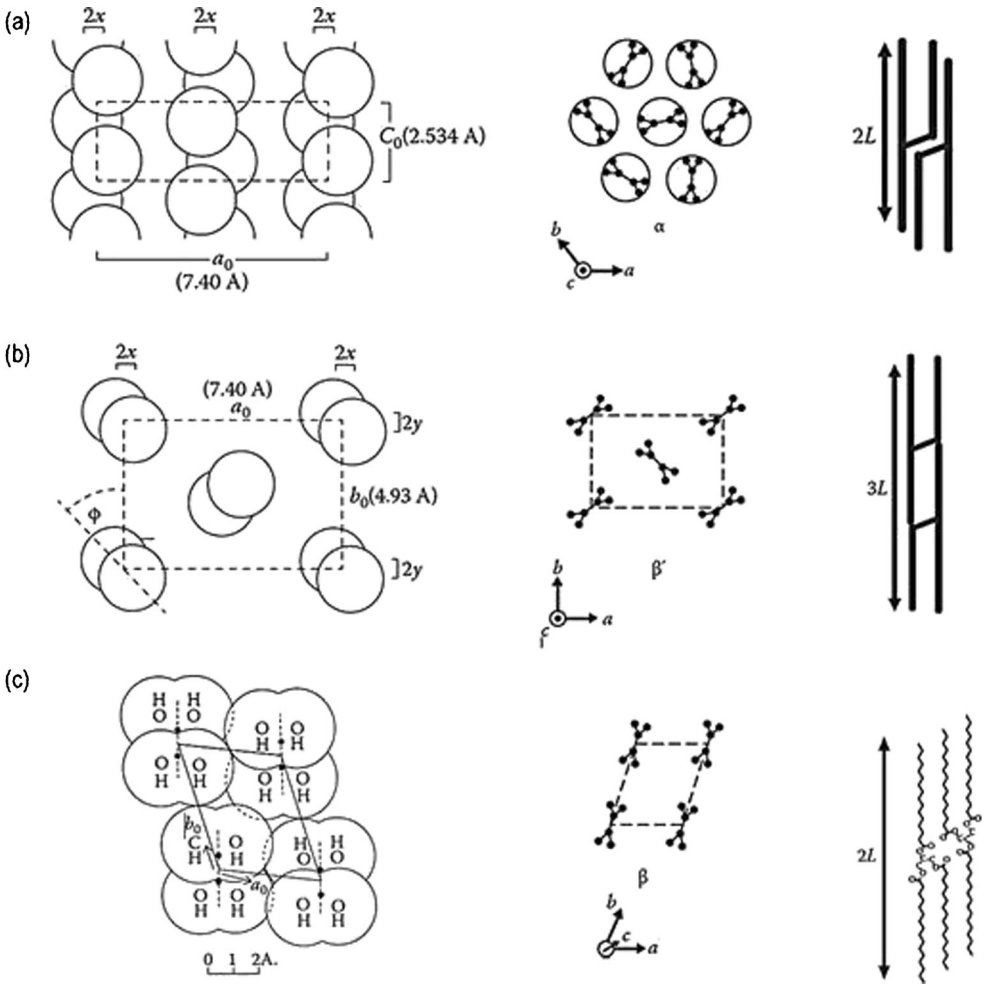

Fig. 2 Spatial projections of the crystalline forms: **a** α, **b** β′ and (**c**) β Packing: *H* hexagonal, *O* orthorhombic, *T* triclinic

TAGs generally crystallize initially in forms α and β′, although form β is more stable. This phenomenon is related to the fact that form β has a higher free energy of activation for nucleation. The polymorphic transformation is an irreversible process going from the less stable to the more stable form (monotropic phase transformation), depending on the temperature and time involved. At constant temperature, the forms α and β′ can become, as a function of time, form β through the liquid–solid or solid-solid mechanisms (Herrera and Marquez Rocha 1996). The transition rate is dependent on the degree of homogeneity of the TAGs. Fats with low variability of TAGs quickly turn into the stable form β. Fats that are the random distribution of TAGs may have the form β′ indefinitely. In addition, factors such as formulation, cooling rate, crystallization heat and level of agitation affect the number and type of crystals formed. However, as fats are complex mixtures of TAGs, at a certain temperature, different polymorphic forms and liquid oil can coexist (Sato 2001).

Fats prone to crystallization in form β′ include the soybean, peanut, canola, corn and olive oils and lard (O'Brien 2008). In contrast, palm and cottonseed oil, milk fat and tallow tend to produce β′ crystals, which tend to persist for long periods (Foubert et al. 2007). In particular, for cocoa butter, there are six polymorphic forms, as a result of its TAG composition, where symmetrical monounsaturated TAGs are prevalent. The characteristic classification of polymorphs of cocoa butter is based on the Roman numbering system (I to VI), in which form I is the less stable one and form V is associated with the crystal habit desirable in chocolates, which can turn into form VI during storage, which offers greater stability. However, usually we can see combinations of this nomenclature with the Greek nomenclature, where the forms V and VI are recognized as β^{V} and β^{VI} (Loisel et al. 1998; Schenck and Peschar 2004). Table 1 shows the crystal tendencies of the more commonly used edible fats and oils.

The crystal structure of fats is important in the formulation of shortenings, margarines and fat products in general, since each crystalline form presents unique properties regarding plasticity, texture, solubility and aeration (Bell et al. 2007). Fats with crystals in form β′ feature increased functionality, as they are softer; provide good aeration and creaminess properties. Thus, form β′ is the polymorph of interest for the production of foods high in fat such as margarine and confectionery and bakery products. For the production of chocolates

Table 1 Classification of fats and oils according to crystal habit (Woerfel 1995)

Beta-prime-type (β′)	Beta-type (β)
Soybean	Cottonseed
Safflower	Palm
Sunflower	Tallow
Sesame	Milk fat
Peanut	
Corn	
Olive	
Coconut	
Palm kernel	
Lard	
Cocoa butter	

with good physical and sensory characteristics, however, form β^V is the desirable polymorph, because it is associated with properties such as brightness, uniformity, characteristic snap and improved shelf life (O'Brien 2008).

X-ray diffraction is used to identify the polymorphism of crystals by determining the dimensions of the crystal unit and sub-cells. Due to the different geometric configurations, the polymorphs diffract the x-rays at different angles. In fats, diffraction in high angles corresponds to short spacings (distances between parallel acyl groups in TAG) of sub-cells and allows the checking of different polymorphs (Campos 2005).

Microstructure

The lipid composition and crystallization conditions influence the crystal habit - different crystalline morphologies are possible. The crystals aggregate into larger structures forming a lattice, which characterizes the microstructural level of a fat. The concept of microstructure includes information about the condition, quantity, form, size, spatial relationship and interaction between all components of the crystal lattice and has enormous influence on the macroscopic properties of fats (Shi et al. 2005).

According to Narine and Marangoni (2005), the microstructural level or mesoscale of the crystal lattice of a fat can be defined as the set of structures with dimensions between 0.5μm and 200μm. Its quantification is obtained primarily through the visualization of its geometry. The levels of structure in a typical crystalline lattice are defined when the fat crystallizes from its complete melting. As nanostructural elements (0.4–250 nm), the TAGs crystallize in particular polymorphic states. Most TAGs crystallizes as spherulites, which implies that the crystalline growth occurs radially. The formed crystals grow up to dimensions of 1 to 4 μm and then join together forming clusters (above 100 μm), through a process governed by heat and mass transfer. The aggregation process continues until a continuous three-dimensional lattice is formed from the amalgamation of these microstructures, trapping the fat liquid phase (Marangoni and Narine 2002). This structural hierarchy was recognized by several researchers (Acevedo and Marangoni 2010; Campos et al. 2010; Mazzanti et al. 2011). However, the arrangement of molecules in the crystalline state also depends on factors such as cooling rate, crystallization temperature and shear rate if required (Tang and Marangoni 2007).

Crystal growth can occur in one, two or three dimensions, characterizing the formation of needle, disc or spherulite-shaped crystals, respectively (McGauley and Marangoni 2002). According to Herrera et al. (1998), the application of fats in food products requires the average diameter of the crystals to be less than 30 μm to avoid the sandiness feeling in the mouth.

Currently, a considerable number of new techniques of microscopy has been used to visualize the surface of foods. In particular, studies on the formation of fat bloom in chocolate are including, in addition to the PLM, techniques such as fluorescence microscopy, scanning electron microscopy, magnetic resonance, atomic force microscopy, laser scanning microscopy and confocal microscopy.

Control of crystallization

The crystallization behavior, polymorphic form and microstructure of fats are due to the combination of the individual physical properties of TAGs and phase behavior of the mixture of TAGs. In general, the specific composition of a fat is one of the most important factors for the final development of the crystalline structure (Vereecken et al. 2009).

The crystallization of fats is a critical factor associated with the structure and properties of most foods. The industrial crystallization process consists of a sequence of steps at different temperatures (undercooling) and application of mechanical force. Three parameters in the crystallization process should be controlled simultaneously in order to obtain good solidification: temperature, crystallization time and agitation rate (O'Brien 2008).

The stability of many processed products is influenced by changes in the physical state of fats and changes in the processes of crystallization, as the crystal growth and nucleation events occur simultaneously at different rates, since they are affected by conditions such as degree and rates of supercooling, viscosity and shear (Toro-Vazquez et al. 2005).

The relative rates of nucleation and crystal growth determine the distribution, form and size of the crystals, parameters that are directly associated with the consistency and texture characteristics. However, during the storage phase, several post-crystallization phenomena may occur, which can considerably affect the properties and stability of foods. These include polymorphic transitions to thermodynamically more

stable phases, formation of new crystals and crystal growth, migration of oil or small crystals. We highlight that, however, such events are not chronological; polymorphic transitions can occur even in the early stages of processing (Himawan et al. 2006).

Additionally, in the processes of post-crystallization, recognized phenomena such as agglutination of adjacent surfaces or sintering, and the spontaneous dissolution, also known as Ostwald ripening, can be seen. The term sintering is described as the formation of solid bonds between the crystals of fat, with the formation of a cohesive network associated with the undesirable increase in hardness of the fat phase. The Ostwald ripening is, in turn, associated with the dissolution of small crystals previously existing in the fat phase and the development of crystals with undesirable dimensions and weaker crystal lattices, which entails the loss of consistency of products (Johansson and Bergenstahl 1995).

In addition, in some specific products, the controlling of crystallization means, above all, avoiding this process, even if it is thermodynamically favored or by processing or storage conditions (Cerdeira et al. 2005). Thus, the control of crystallization and polymorphic transitions in fats consists of a factor of fundamental importance for the food industry.

Crystallization of fats of industrial relevance

Cocoa butter

Cocoa butter is an important component used in the manufacture of chocolates. It represents the solid phase of the product, serving as dispersant matrix for sugar, milk and cocoa solids. Cocoa butter is responsible for various characteristics of the final product quality, such as hardness and snap at room temperature, complete melting in the mouth, brightness, contraction during demoulding and fast release of aroma in tasting. Moreover, cocoa butter is one of the most expensive ingredients of chocolate, representing 25 to 36 % (w/w) of the cost of the end product (Hindle et al. 2002).

Cocoa butter is composed of approximately 97 % of TAGs, mainly the saturated-unsaturated-saturated type. Among these, the TAG species 1-palmitoyl-2-oleoyl-palmitin (POP), 1-palmitoyl-2-oleoyl-stearin (POS) and 1-stearyl-2-oleoyl-stearin (SOS) represent between 80 and 90 % of all TAGs. Small amounts of MAGs and DAGs (approximately 2 %), free fatty acids and phospholipids are part of the composition of crude cocoa butter (Lipp and Anklan 1998).

The differentiated thermal and structural behavior of cocoa butter reflects its TAG composition, as all majority TAGs in its composition have complex polymorphism. The polymorphism of cocoa butter is directly linked to the quality of the product and the processing performance. The crystal modifications in cocoa butter, except for form β^{VI}, can be obtained directly from the liquid state, in proper cooling conditions. This fact suggests that the $\beta^{V} \rightarrow \beta^{VI}$ transition is mediated only by solid-solid transformation (Garti et al. 1986).

In the production of chocolate, cocoa butter must be pre-crystallized or tempered before the molding or coating steps. Tempering, characterized by certain protocols time x temperature, is employed to promote the crystallization of the more stable polymorph. In chocolate, tempering should induce the formation of nuclei of type β^{V} crystals, which give the desirable characteristics to the product (Loisel et al. 1998). The tempering process begins with the complete melting of the fat phase of the chocolate, at 40 °C. Then, there is the controlled cooling, stirred, to induce fat crystallization. The cooling rate should be close to 2 °C/min up to a temperature of approximately 28 °C. In this step, besides the formation of the desired type β^{V} crystals, there is also the formation of smaller amounts of unwanted crystals, e.g. type β', which is unstable and has a lower melting point, which are eliminated with a subsequent heating of the mass at 30–32 °C (Quast et al. 2007). This procedure is the usual technique to control the polymorphic crystallization of cocoa butter (Sato 2001).

The tempering is the critical step of processing, not only regarding the quality of the chocolate produced, but also regarding economic terms, as problems in its control (temperature and uniformity) has caused the need for reprocessing, burdening energy costs and area use in industrial plants. Chocolates with different ingredients often require different tempering protocols. Moreover, improperly tempered or crystallized chocolates are associated with the fat bloom phenomenon, considered the main problem in quality in chocolate and confectionery industry, which leads to rejection by the consumer and considerable damage in the marketing of these products (Depypere et al. 2009).

The formation of fat bloom in chocolate adversely affects the appearance and texture attributes, since it generally promotes the formation of whitish and non-uniform surfaces. The generally accepted perception is that the visual fat bloom is a function of the migration of the cocoa butter to the surface, which is deposited in the form of crystals with dimensions between 4 and 5 μm. However, a variety of fat bloom types may occur, depending on the type of chocolate and the conditions of storage, and such variation further hinders the understanding of this phenomenon (Kinta and Hatta 2007).

Although many studies have been devoted to fat bloom, its causes and forms of remediation are not yet fully addressed in the technical literature. It is considered that the fat bloom in chocolate can be resulted from various situations. Inefficient tempering, for example, is responsible for its quick development. Fat bloom is also verified when fats incompatible with cocoa butter are added to chocolate. Other common causes are incorrect cooling of tempered chocolates and temperature

fluctuations during storage. The specific mechanism through which it occurs is still unknown, although several theories have been proposed. The most accepted theory is that fat bloom is formed because of the polymorphic transition of cocoa butter. The transformation of unstable crystals into stable crystalline elements would result in fat bloom, primarily associated with the $\beta^{V} \rightarrow \beta^{VI}$ transition. Recently, another visual form of fat bloom characterized by lightly colored surfaces was reported. In this differentiated type of bloom, the formation of crystalline nuclei in the form β^{V} was not observed (Lohman and Hartel 1994; Lonchampt and Hartel 2004).

During the production of chocolate, in addition to the desirable polymorphism, parameters such as the proportion of solid fat present, number and size of crystals, crystal morphology and microstructure are fundamental in determining the finished product, modulating the rheological and mechanical properties of chocolate (Afoakwa et al. 2008). To conclude, the production of good quality chocolate is modulated by the proper manipulation of cocoa butter, associated with favorable storage conditions. However, the costs associated with the tempering process, as well as the difficult stabilization of the cocoa butter crystallization during and after processing are still problematic factors for the industrial sector.

Palm oil

Palm oil is obtained from the mesocarp of the fruit *Elaesis guineensis*. It is semi-solid at room temperature, consisting mainly of TAGs of palmitic and oleic acids. Palm oil is the world's largest vegetable oil used in the food industry (Oil World 2013).

Compared to other vegetable oils, palm oil has a unique and differentiated fatty acid composition, containing similar percentages of saturated and unsaturated fatty acids. Also, it has significant saturated fatty acid content (10 to 16 %) in the position *sn*-2 of TAGs, in addition to significant levels of palmitic acid (44 %). Besides these features, palm oil has small percentages of MAGs and DAGs as minority components, which are produced during the maturation of the palm fruits and oil processing. The DAGs, specifically, correspond to 4–8 % of the composition of the palm oil, with variations according to geographical origin and processing conditions. The removal of these compounds, however, is difficult even under optimum conditions of refining (O'Brien 2008; Okawachi and Sagi 1985).

Interesterified palm oil and palm stearin, obtained through the respective interesterification and fractionation processes, represent fat bases with extensive use by the food industry. The hard fraction of palm oil, known as hard palm midfraction, is usually employed as an ingredient in cocoa butter equivalents (CBEs), being characterized by the high content of the TAG species 1-palmitoyl-2-oleoyl-palmitin (POP) and fast melting between 30 and 35 °C, as cocoa butter (Hashimoto et al. 2001).

The crystallization behavior of palm oil is extremely important from the commercial point of view, due to crystal habit β', which, associated to its characteristics of plasticity, ensures its application in margarines, spreads, bakery and confectionery fats and general-purpose shortenings. The functional properties of palm oil and its fractions are strongly related to their composition and to the amount and type of crystals formed on the application temperature range. However, the crystals of palm oil need a long time for the $\alpha \rightarrow \beta'$ transition, a factor considered as inappropriate from the perspective of industrial processes. The resistance to change into β' is mainly attributed to DAGs. Recent studies on the interactions between TAGs and DAGs of palm oil during crystallization show that the latter have deleterious effect on the characteristics of crystallization, with intensity proportional to the concentration of these minor lipids in palm oil or its fractions (Che Man et al. 2003; Chong et al. 2007). According to Watanabe et al. (1992), the negative effect of DAGs on the crystallization of palm oil would 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 the industry is its post-processing stability. Palm oil is often associated with hardening problems during storage. In some products based on this raw material, there is the undesirable growth of crystals, which results in sandiness texture and low spreadability (Omar et al. 2005). These crystalline forms can reach dimensions greater than 50 μm in a few weeks of storage, causing the non-uniformity of the end products (Watanabe et al. 1992). In margarines, specifically, there is the formation of crystal clusters with an average diameter between 0.1 to 3 mm, which can easily be observed with the naked eye (Garbolino et al. 2005).

Tanaka et al. (2007) verified that the main TAGs of palm oil, 1-palmitoyl-2-oleoyl-palmitin (POP) and 1-palmitoyl-diolein (POO), have limited miscibility among themselves, which results in the formation of large POP crystals enveloped by POO. When these clusters are formed, there is the junction of other saturated TAGs, in a process that promotes the $\beta' \rightarrow \beta$ transition. Therefore, to ensure the stability of the polymorph β' in products based on palm oil is a matter of great industrial interest, given the vast economic importance associated with the use of this raw material.

General purpose fats

Most natural oils and fats have limited application, imposed by their particular composition in fatty acids and TAGs. This way, oils and fats for various industrial applications are chemically modified, through hydrogenation or interesterification, or physically modified, through fractionation or mixture (Erickson 1995). Although used for a long period, the partial

hydrogenation results in the expressive formation of trans fatty acids, associated with negative health effects (Hunter 2005).

Worldwide, the controversial issues about the role of *trans* fatty acids in food caused progressive modifications in legislation, aiming at the inclusion of more information for consumers, requiring the declaration of the levels of these components on the nutrition labeling of foodstuffs. In response, the industries have opted for the progressive replacement of *trans* fat in various products, through the development of fat bases with economic viability and functionality equivalent to partially hydrogenated fats, without increasing the content of saturated fatty acids in foods (Ribeiro et al. 2007).

In this sense, interesterification proved to be the main alternative for obtaining plastic fats with low levels of trans isomers or even absence of these compounds. Particularly, the chemical interesterification of liquid oils with fully hydrogenated oils (hardfats) is currently the alternative of greater versatility to obtain zero trans fats, producing fat bases with favorable characteristics to prepare general-purpose shortenings (Ribeiro et al. 2009). The use of blends, i.e. mixtures of fats with different physical properties, and fractionation are also additional alternatives for obtaining fat bases with proper plasticity and physical characteristics to be used in several products, although with potential limited by the chemical composition of the raw materials (Foubert et al. 2007).

Although the processes of interesterification, fractionation and blending are very functional under the technological point of view, the replacement of partially hydrogenated fats in food products, mainly in shortenings and confectionery, is currently a challenge, as suitable crystallization and texture properties are difficult to obtain in the absence of trans fatty acids (Reyes-Hernandez et al. 2007).

Especially, the appropriateness of the crystallization kinetics of these fat bases is of is of paramount importance for their use can be adjusted to the limitations of industrial processes and to improve the control of the processing steps involving the recrystallization of the fat fraction, ensuring the quality of the end product (Foubert et al. 2006). Otherwise, processing times and equipment already standardized need to be changed according to the characteristics of the fat used. This fact has become particularly important as new fat bases began to replace partially hydrogenated fats in most industrial applications, mainly in the production of biscuits and bakery products, in which it was noted that fats with the same apparent solid profile presented very different crystallization properties (Bell et al. 2007). 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 through changes in the process of nucleation of crystals (Herrera et al. 1999). According to Minal (2003), 0.1 % of sodium methoxide catalyst, employed for randomization, can produce between 1.2 and 2.4 % of MAGs+DAGs. Since the typical content of the catalyst used industrially varies between 0.1 and 0.4 %, the resulting levels of these minor lipids can be greater than 9 %. Although minor lipids have influence on the properties of crystallization of these fats, their complete removal is still difficult and costly, especially on a large scale (Metin and Hartel 2005).

Considering that this replacement process is relatively recent, the crystallization behavior problems because of the non-suitability of new fat bases are numerous and exacerbated, mainly because of regional climatic differences and conditions of transportation and storage. In this context, we can highlight problems like undesirable polymorphic transitions, exudation of oil, development of fat bloom, formation of crystalline clusters, as well as fat bases with maximum content of solid fat or induction periods incompatible with certain industrial applications. Studies on the modification, stabilization and control of the crystallization of these materials thus have crucial importance for the development of the industry of edible oils.

Crystallization modifiers in oils and fats

From the considerations above, the modification, control and/or stabilization of the crystallization and polymorphic transitions of fat raw materials can be done mainly through three alternatives, used individually or combined, according to the requirements of each fat basis: (i) removal, addition or fractionation of minor lipids in fat bases; (ii) use of nucleating agents to modulate the process of crystallization (seeding); (iii) dynamic control of the crystallization in lipid systems through the use of emulsifiers.

Historically, it was understood that the crystalline modification in oils and fats would be linked primarily to physico-chemical changes provided by processes such as hydrogenation, interesterification, fractionation and blending, as well as the use of specific time x temperature protocols (Omar et al. 2005).

The alternatives for modification, control and/or stabilization of crystallization here mentioned are based on recent research studies on the technology of oils and fats, which in recent decades showed great advances by employing highly sensitive analytical techniques, which enabled evaluations under crystallographic, micro-structural, and kinetic perspectives which were unknown before in the science of lipids (Sato and Ueno 2005).

Removal, addition or fractionation of minor lipids

Minor lipids (ML) include lipids of greater polarity and with an amphiphilic structure, such as DAGs, MAGs, free fatty

acids, phospholipids and sterols. These constituents have been considered molecular agents that affect crystallization. In some cases, the presence of ML can promote crystallization, while, in some systems, there is the effect of inhibition (Metin and Hartel 2005). According to Toro-Vazquez et al. (2005), these compounds modulate all the crystallization process, from the nucleation to the post-crystallization events.

The action of ML on the crystallization of fats is the subject of several recent studies. Some of them evaluate the ML of a given set source; others are directed to the evaluation of a specific component, such as DAGs or phospholipids. Most research studies, however, have focused DAGs, class of ML that is predominant in oils and fats (Mazzanti et al. 2004).

There are some potential mechanisms described in the literature that support the hypothesis that ML can affect crystallization. It is considered the occurrence of interactions of ML with crystals of TAGs in growth, which generates a structural competitive effect or permanent incorporation in the crystalline structure, in order to prevent or enhance growth. In this case, ML could also limit the transference rate of TAGs to the sites of incorporation in the crystalline structure. Through these processes, ML would affect the properties of crystallization rate, polymorphic forms and microstructure of crystals, through the preferential inhibition or promotion of the development of certain crystal faces. Some authors also associate the effect of ML to the heterogeneous nucleation induction, according to the proposition that these compounds are organized separately in micelar structures, acting as bases for the nucleation process. However, the distinction of these effects and their selectivity between crystalline growth or nucleation phases is not yet fully established in the literature, being a subject of great interest in the science of lipids (Foubert et al. 2004; Wright and Marangoni 2002; Metin and Hartel 2005).

In general, the effects of the various ML on the crystallization of fats show that this process can be controlled by adding, removing or even selectively fractionation components between the glycerol classes or even within the same class of compounds (Oh et al. 2005).

Minor lipids

The effect of the set of typical ML of a specific fat has been recently evaluated in literature. Toro-Vazquez et al. (2005) studied the effect of removing ML from cocoa butter. Purified cocoa butter exhibited a shorter time for crystallization and higher rate in the polymorphic transitions, especially in relation to the $\alpha \rightarrow \beta'$ transition. However, the removal of these compounds did not modify the mechanism of crystalline growth. Bunjes et al. (2003) reported that the presence of ML slowed the $\alpha \rightarrow \beta'$ transition into tripalmitin (PPP). This behavior was attributed to the formation of less ordered polymorph α, because of the ML-PPP interactions. According to Mazzanti et al. (2004), the removal of ML prevents the accommodation of a wide variety of molecules during the crystal formation. Thus, TAGs in purified fats would be free to be accommodated in the more stable polymorphic phase, this way accelerating the $\alpha \rightarrow \beta' \rightarrow \beta$ transitions.

In studies with milk fat, Wright et al. (2000a, b) and Herrera et al. (1999) verified that the ML slowed the nucleation period at temperatures above 25 °C. However, their observations on the crystal growth rate are contradictory and were attributed to differences in composition. Mazzanti et al. (2004) found that the ML present in milk fat slowed the beginning of crystallization and reduced the rate of growth of the crystals, promoting, in addition, the instability of form β'.

Studies of the crystallization of cocoa butter with added milk fat (10 %) were performed by Tietz and Hartel (2000). The evaluations were made for the complete removal and natural (2.5 % w/w) and duplicate (5.0 % w/w) levels of ML in milk fat. Removing the ML resulted in an increased nucleation period, formation of primary and secondary irregular crystals, with inclusion of liquid fat and rapid formation of bloom in chocolates produced with this fat basis. ML in natural levels have been associated with the formation of spherical and uniform crystals, while the increase of concentration of these compounds produced accelerated crystallization. The authors suggest that ML act as catalytic sites of nucleation when present in low levels and may interfere with crystallization in high concentrations.

In general, the latest research studies show some degree of consensus that ML in natural or slightly higher concentrations are associated with the uniformity of crystals and reduction of the phenomenon of fat bloom; the precise effect on the crystallization and polymorphic habit is still controversial, according to the different results verified for the same type of raw material and the paucity of studies on the joint action of ML (Metin and Hartel 2005).

Phospholipids

Phospholipids crystallize at higher temperatures compared to TAGs, and they can act as crystallization nuclei. In studies of nucleation in cocoa butter, Arruda and Dimick (1991) showed that isolated crystalline nuclei presented in their composition levels 12 times higher of phospholipids compared to the concentration of phospholipids originally present on this fat. This study suggested that phospholipids, particularly phosphatidylcholine and phosphatidylethanolamine, develop crystallization nuclei for the subsequent crystallization of TAGs. Chaiseri and Dimick (1995) associated the nucleation rate of cocoa butter with the polarity of phospholipids. High concentrations of polar phospholipids, such as lysophosphatidylcholine and phosphatidylinositol, were related to slow nucleation rates, whereas for rapid nucleation low concentrations of these compounds and significant levels of

phosphatidylcholine were observed. Additional results indicated that the removal of phospholipids by refining had the effect of decreasing the crystallization rate of cocoa butter, with increase induction period in comparison to the original raw material, therefore suggesting that phospholipids are necessary elements to supply the crystallization nuclei of cocoa butter.

The effect of the addition of phospholipids on the crystallization of refined cocoa butter was evaluated by Lawler and Dimick (2002). The incorporation of 0.1 % of phosphatidylcholine promoted increase in the crystallization rate of the samples. In addition to this effect, the authors observed an increase of solid fat content of cocoa butter after tempering, suggesting that the addition of certain phospholipids, in appropriate concentrations, can handle the crystallization and assist in the development of polymorphic forms that are more stable in cocoa butter. Vanhoutte et al. (2002) reported that the increase in concentration of phospholipids in milk fat slowed the onset of crystallization. A similar effect was observed by Miura et al. (2006), in a study on the crystallization of pure butter oil containing added phospholipids.

The incorporation of different lecithin, at concentrations of 0.1, 0.5 and 1.0 % (w/w), on the crystallization behavior of palm oil and an interesterified fat, indicated that the added lecithins showed tendency to slow the formation of fat crystals. This may prove to be one of the solutions in industrial processes where this effect is desired, when replacing *trans* fats by zero *trans* fats in food processing and stability (Correa et al. 2011).

Smith (2000) also verified that phospholipids, added at concentrations of 0.1, 0.2, 0.5 and 1 % (w/w), showed interactions with the nucleation and crystal growth in palm oil, trilaurin (LLL) and tristearin (SSS). The study showed that the types of interaction phospholipids-TAGs would be dependent on the chemical structure of phospholipids and the chain size similarity between these compounds. Some phospholipids showed to be nucleation inhibitors, while others had pronounced effect on the crystallization rate, such as the studies mentioned above. Additionally, changes were observed in the shape, size and polymorphism of the crystals, in all concentrations of phospholipids evaluated.

Although the isolated function of phospholipids on the crystallization behavior of fats is not yet completely understood, some events are related to the presence and/or addition of these compounds, including: the formation of nuclei or crystallization seeds, microstructural changes and modifications of the typical processes of nucleation and crystal growth of certain lipid materials. The findings, still contradictory, reported in the literature, can be explained by the natural chemical diversity of the evaluated fats, and as a consequence the use of different instrumental methodologies and supercooling conditions (Toro-Vazquez et al. 2005).

Diacylglycerols (DAGs)

DAGs represent the class of ML of greatest interest to the studies of crystallization of lipids, as they occur in higher concentrations in virtually all vegetable or animal fats (O'Brien 2008).

Studies on the action of DAGs have primarily focused milk fat. Wright and Marangoni (2002) evaluated the effect of the complete removal of ML from milk fat and subsequent addition of DAGs of these components, at a concentration of 0.1 % (w/w). The DAGs slowed the crystallization process, with increased in the induction time, but they did not modify the microstructure of the milk fat. Foubert et al. (2004) reported that the addition of 0.5 and 1.0 % (w/w) of diestearin and diolein to milk fat showed dependent effects on temperature and concentration. The type of fatty acid determined the effect of DAGs on crystal growth and nucleation: diestearin induced nucleation at low temperatures and modified crystal growth at high temperatures; diolein had an effect only on nucleation, in a wide temperature range.

Tietz and Hartel (2000) verified that the 1,2-diacyl-glycerols in a blend of cocoa butter/milk fat slowed the crystallization; in contrast, the 1,3-diacyl-glycerols promoted a significant change in the crystallization rate. According to the authors, this fact shows that DAGs at specific levels may have greater importance in comparison to the total concentration of DAGs in a lipid system. Similarly, Chaiseri and Dimick (1995) reported that the presence of DAGs high in stearic acid promoted fast nucleation of cocoa butter.

Siew and Ng (1999) observed that palm oil DAGs inhibited the process of nucleation and hampered the crystal growth of TAGs. In palm olein, dipalmitin and 1-palmitoyl-2-oleoyl-acylglycerol had positive and negative effects on the crystallization rate, respectively, while diolein showed a neutral effect. Long *et al*. (2005) suggest that the precise effect of DAGs on the crystallization of palm oil is dependent on their concentration and chemical structure. This proposition shows agreement with other studies in literature. Smith and Povey (1997) reported that the most significant delays on the crystallization of trilaurin were observed when there was a similarity between the chain size of the added DAGs and lauric acid. In a study of crystallization of coconut oil, Gordon and Rahman (1991) verified that the addition of dilaurin increased the crystallization induction period; the addition of diolein showed no effect on this parameter. Studies of Martini and Herrera (2008) evaluated the influence of incorporation of saturated and unsaturated DAGs to different blends of palm oil/palm kernel oil/soybean oil/sunflower oil. DAGs modified the shape and number of crystals, which affected the solid fat content. DAGs with similar chemical composition to the chemical composition of the blends slowed or inhibited crystallization more efficiently.

Saberi et al. (2011) studied the effect low and high concentrations of palm DAGs on the crystallization kinetics of palm oil. The addition of 2 and 5 % of DAGs decreased (negligibly and significantly, respectively) the rate nucleation, the rate of crystallization and the mechanism of crystal growth in palm oil. According to the authors, low concentration of DAGs (10 %) can be used as a stabilizer agent of β′ polymorphous in palm-based products. However, the addition of 30 and 50 % of DAGs significantly increased the rate of nucleation and crystallization, and it also significantly changed the crystal microstructure of palm oil. From the standpoint of industrial applications, the use of high concentrations of DAGs (40 %) in palm-based margarines might be interesting to inhibit post-crystallization hardening in such products.

Therefore, regarding the action of DAGs on the nucleation and crystal growth rates, literature shows that this glycerol class can have a promoting or inhibiting effect on crystallization, primarily as a function of compatibility between its composition and the composition of the lipid raw materials. According to Wright and Marangoni (2002), the ability of the DAGs as modifiers of the crystalline behavior of TAGs is primarily related to the similarity in the chemical composition between these glycerol classes. The studies presented so far suggest that the parameters that define this degree of similarity are the isomerism or stereospecificity of DAGs and their composition in fatty acids, in relation to the chain size and saturation. Also, the effect of the addition of DAGs is dependent on their concentration and more pronounced at low degrees of supercooling.

In general, the polymorphic stability of fats increases significantly with the addition of DAGs, even at low concentrations. Again, their molecular structures, in particular the chain size of their fatty acids and position in the glycerol molecule, show importance for this purpose (Oh et al. 2005). According to Wright et al. (2000a, b), the structural complementarity between the DAGs and TAGs molecules would allow the cocrystallization of these compounds, stabilizing polymorphs and avoiding undesirable transitions. So far, studies indicate that the 1,2-diacyl-glycerols slow polymorphic transitions more effectively than their 1,3-diacyl-glycerols isomers, a difference attributed to the fact that the first preferably exhibit orthorhombic packing, while the later exhibit triclinic arrangement (Oh et al. 2005).

In studies with palm oil, Berger and Wright (1986) showed that α polymorph showed lifetime from 16 to 55 min with the addition of 6.4 and 20 % of DAGs, respectively. Under the same crystallization conditions, Chong et al. (2007) reported that the lifetime of the polymorph α was reduced by half when removing these compounds.

The addition of 5 % of DAGs was effective in slowing the β′ → β transition in margarines, according to a study of Hernqvist and Anjou (1983). In cocoa butter, the presence of DAGs inhibited the $\beta^{V} \rightarrow \beta^{VI}$ transition, according to Tietz and Hartel (2000). In rapeseed oil with high levels of stearic acid and a small amount of erucic acid, the addition of diestearin showed the greatest stabilizing effect on β′ polymorph, when compared to dipalmitin and diecosanoin. The use of 1,2-diacyl-glycerols had greater effect on the stability of the forms α and β′ than 1,3-diacyl-glycerols (Hernqvist et al. 1981).

Some studies also investigate the effect of adding DAGs to pure TAGs. Smith et al. (1994) reported that the addition of 1,2-dilaurin to trilaurin showed a greater effect on the β′ → β stabilization than the addition of 1,3-dilaurin. Oh et al. (2005) evaluated the influence of incorporating dipalmitin, diestearin, diolein and dilinolein (5 % w/w) to tristearin. DAGs showed a stabilizing effect in the α → β′ transition during storage at 53 °C, with maintenance of the α form, and stabilization of the β′ →β transition in storage at 59 °C.

A recent study suggested that the addition of DAGs changed the crystallization process of tristearin (SSS), with changes in the crystallization and melting profiles. The melting curve of pure tristearin presented two endothermic peaks that correspond to the polymorphic forms α and β, and a exothermic peak between the two endothermic ones, corresponding to the events of the polymorphic transition α-β′-β. The addition of diestearin in the system increased the peak area of polymorphic form α compared to pure SSS, while form β had its peak area reduced. The addition of dipalmitin increased both peak area α and β. The presence of diolein caused the peak area concerning form α to be reduced, while peak area β was increased. The exothermic peak was also affected by the presence of DAGs. The results indicate that the addition of OO promotes the polymorphic transition, whereas PP and SS slow the polymorphic transition to the more stable crystalline form (Silva et al. 2014).

Other properties described in the literature on the influence of DAGs on the crystallization of fats include changes in the shape and number of crystals, neutral effect on melting point and solid fat content, decreased tempering temperature and consistency of cocoa butter (Metin and Hartel 2005).

Monoacylglycerols (MAGs)

The MAGs are present in smaller amounts in fats, and few studies are available on the effect of these compounds on the crystallization behavior of lipid systems. The studies available so far show acceleration of fat crystallization, changes in the shape and number of crystals, as well as decreased consistency and solid fat content in an extensive temperature range (Foubert et al. 2004).

Sambuc et al. (1980) investigated the effects of MAGs in the crystallization of various vegetable fats. The addition of 4 % of the monopalmitin/monostearin blend decreased the induction period for all samples evaluated. Smith et al. (1994) showed that the incorporation of monolaurin accelerated the

crystallization of trilaurin, with additional decrease in the size of the crystals. Miura et al. (2002) reported the effect of MAGs from myristic, palmitic, stearic, lauric and behenic acids (0.4 % w/w) on the crystallization behavior of palm oil. The content of palm oil solid fat decreased with the addition of MAGs from myristic, palmitic and stearic acids; MAGs from lauric and behenic acids showed no effects on crystallization.

Addition of nucleating agents - seeding

The knowledge on the mechanisms to control the crystallization of fats promoted the development of a new proposal with great potential to modulate and substitute the conventional processes of crystallization and tempering of fats for various industrial purposes, based on the addition of nucleation agents, a technique known as seeding. This alternative is based on the fact that the crystallization of fats can be promoted by adding solid material with properties of nucleation agents – or crystallization seeds. The incorporation of crystallization seeds into liquid fats may promote two effects associated with the control of crystallization: availability of numerous additional nuclei (known as ready-made nuclei) and/or surfaces for crystal growth. Moreover, another technical advantage associated with the use of nucleating agents is related to their great potential as promoter of specific polymorphic forms. Active nucleation agents with specific crystal habit may induce crystallization of fats in the desirable polymorphic forms, as the information for the crystalline packing is provided by the seeds that control this process (Padar et al. 2008; Metin and Hartel 2005).

From a thermodynamic perspective, the use of crystallization seeds is ideal for directing the crystallization in fat bases. The binding of TAG molecules to a pre-existing crystal face is favored, without the energy requirement to create a crystal nucleus (Lonchampt and Hartel 2004). However, in the process of seeding, the temperature control is critical to the permanence of stable crystalline seeds. Additionally, the extension of its effect depends on parameters such as ratio of the mass of the solid material incorporated and the mass of the melted fat to be crystallized, inoculation temperature and cooling rate (Debaste et al. 2008).

Recent studies indicate the use of crystallization seeds as the alternative with greater technological potential for replacement or improvement of conventional tempering, used in the production of chocolates. This technics would solve the problems of insufficient tempering, incomplete crystallization, heterogeneous nucleation during cooling, crystalline instability in temperature fluctuations during storage and, consequently, prevention or inhibition of fat bloom. Additionally, the process of seeding exhibits favorable effects as a crystallization accelerator of palm oil and as a modulator of the crystallization kinetics of fat bases for specific purposes (Smith et al. 2008). Generally, the following advantages are attributed to the use of the seeds of crystallization: reduced sensitivity to variations in temperature, fast solidification and superior fat products (Lonchampt and Hartel 2004).

The crystallization agents used in the seeding technique consist of saturated or unsaturated TAGs. For the crystallization of cocoa butter, particularly, the use of symmetrical disaturated TAGs, with a higher tendency to the formation and permanence of the polymorph β^{V}, is recommended. The use of TAGs as active nucleation agents is also associated with the anti-bloom effect, by avoiding the $\beta^{V} \rightarrow \beta^{VI}$ transition (Smith et al. 2008). Pure TAGs are potential nucleation agents in fats for bakery and general-purpose shortenings as enhancers of the process of crystallization and controllers of the polymorphic form of these raw materials. On the fractionation of palm oil, process improvements have been based on the addition of tripalmitin (PPP) to liquid fat, facilitating the crystallization of 1-palmitoyl-2-oleoyl-palmitin (POP) (Vereecken et al. 2009). Basso et al. (2010) evaluated the addition of tripalmitin on the crystallization features of palm oil. Campos et.al (2010) studied the effects of the addition of tristearin and trilinolein to cocoa butter. The modifying potential of tripalmitin and tristearin in safflower and soybean oils was reported by Dibildox-Alvarado et al. (2010).

According to Sato (2001), specific molecular interactions between materials of the crystallization agents and the fat to be crystallized are prerequisites for the seeding effect, in terms of polymorphic correspondence, similarity of aliphatic chain and thermal stability. Regarding the polymorphic matching, the seed material must have the same polymorphic form of the desired polymorphic form for the nucleation of the mother phase, usually β' or β. The similarity of the aliphatic chain involves two meanings: chain length and chemical structure of fatty acids. Takiguchi et al. (1998) suggest that the chain length of the fatty acids crystallization seeds must not differ by more than four carbon atoms in relation to the predominant fatty acid in the mother phase. The chemical structure of the fatty acids refers to the degree of saturation. When the mother phase is made up of a blend with a large amount of unsaturated TAGs, crystallization seeds without unsaturated fatty acids will be less effective. Finally, the thermal stability is simply due to the fact that the seeding material should not melted in the liquid phase of the fat at the inoculation temperature. Therefore, the melting point of crystallization seeds must be higher than the melting point of the fat being crystallized. Consequently, the selection of materials with proper polymorphism and compatible melting point is essential for the seeding process (Himavan et al. 2006).

Despite the huge potential of this technics to modify crystallization of fats, few studies are found in literature. Hachiya et al. (1989) proved that the crystallization nuclei formed spontaneously in cocoa butter developed by grouping the

TAG species 1-stearyl-2-oleoyl-stearin (SOS) constitute surfaces for aggregation of other TAGs. Sato (2001) evaluated the performance of the TAGs 1-stearyl-2-oleoyl-stearin (SOS), 1-behenyl-2-oleoyl-behenyl (BOB) and tristearin (SSS), at variable concentrations between 0.1 and 5.0 % (w/w) as crystallization seeds of cocoa butter. The ideal outcome was obtained for BOB, having the author concluded the following advantages of the seeding process for the production of chocolates: (i) accelerated crystallization of cocoa butter directly in form β^V; (ii) no need for the tempering process; (iii) significant improvement of chocolate stability to the fat bloom. In practice, after inoculation of the TAGs in the liquid chocolate mass, only cooling to approximately 15 °C was required, without need for any additional step. The effect of BOB (at concentrations of 0.5, 1.25 and 2.5 %) on the inhibition of fat bloom in dark chocolate was confirmed by Walter and Cornillon (2001).

Van Malssen et al. (2001), cited by Schenk and Peschar (2004), patented a technique for the production of chocolates that replaces the traditional tempering by using crystallization seeds in form β^V, obtained by spray freezing. The chocolates presented excellent brightness and good shelf-life stability. Pore et al. (2009) and Gwie et al. (2006) reported the production of crystallization seeds with tripalmitin and cocoa butter, also by the spray freezing process. Vereecken et al. (2009) evaluated the potential of combining different TAG as crystallization seeds. The authors concluded that the best nucleation agents were formed by blending crystals tripalmitin (PPP) and 1-palmitoyl-2-oleoyl-palmitin (POP) and tristearin (SSS) and 1-stearyl-2-oleoyl-stearin (SOS). The studies on the effect of the seeding on the crystallization of fats are still scarce, in relation to the type of fat being crystallized and to the nature of the materials with favorable characteristics for effective action as crystallization seeds. Few TAG species were tested, as well as their combined action or synergism as crystallization regulators.

Current research studies indicate the use of fully hydrogenated oils, or hardfats, as potential crystallization modifiers of oils and fats, in order to obtain better quality products and industrial processing with significant cost reduction. Oliveira et al. (2011) found that the addition of hardfats promoted drastic changes in the of crystallization profile of palm oil and, increasing the consistency of this raw material. The incorporation of 1 % of hardfats from palm, cottonseed and soybean oils into palm oil promoted a significant reduction in induction time of crystallization, which decreased from 34 min to 29, 27 and 21 min, respectively. Recent study by Ribeiro et al. (2013), showed that use of hardfats from palm, soybean, cottonseed and crambe oils presents effective potential as modifiers of the physical properties of cocoa butter, promoting increased hardness and changes in microstructure of this raw material. The results guide for use of these hardfats, added at low concentrations, as active agents in lipid modification processes, a highly viable option for situations in which the adequacy of the physical properties of cocoa butter is required.

Emulsifiers

Emulsifiers are functional additives of utmost importance in the food industry. They are amphiphilic molecules, usually with long hydrocarbon chains, characterized by simultaneous hydrophilic and lipophilic properties. Beyond their emulsifying and stabilization functions, emulsifiers can modify the solid phase behavior of a food product, giving it specific benefits. In foods high in fat, emulsifiers can be used to control or modify the crystallization properties of the fat phase. The study of the effects of emulsifiers in lipid systems is of great interest for the improvement of industrial fat bases, particularly regarding fats for use in chocolates, confectionery and bakery. However, the role of these compounds as crystallization modifiers in natural and commercials fats has not been completely elucidated in literature (Hasenhuettl 2008). So far, the vast majority of studies on the use of emulsifiers as modifiers of the fat crystallization process were conducted with fully hydrogenated oils, model-systems or pure TAGs, and do not reflect, therefore, the need to control the crystallization of fats of industrial use (Rousseau et al. 2005; Cerdeira et al. 2006).

Emulsifiers with different hydrophobic properties can affect the dynamics of crystallization of fats and oils, accelerating or slowing down this process, as well as the polymorphic transitions. Also, emulsifiers can act as inhibitors of fat bloom. These compounds promote changes in the surface properties of lipids, resulting in changes related to the size and morphology of crystals and crystalline density (Garti 2002).

In general, the effect of emulsifiers is related to different crystal organizations and the creation of imperfections. Some of them may slow the transformations through steric hindrance, while others promote these transformations by favoring molecular displacements (Aronhime et al. 1987). Two different mechanisms have been described in literature in order to interpret the effects of emulsifiers on the crystallization of fats. The first one refers to the performance of these additives as heteronuclei, accelerating the crystallization through the direct catalytic action as impurities. During crystal growth, the emulsifiers would be adsorbed on the surface of the crystals and therefore would change the rate of incorporation of TAGs and the crystal morphology. The second mechanism considers that TAGs and emulsifiers would be likely to suffer cocrystallization because of the similarity between their chemical structures. Thus, the structural dissimilarity would also entail delay on the nucleation and possible crystal growth inhibition (Cerdeira et al. 2003; Garti 2002). According to this mechanism, the emulsifiers are associated with the TAG

molecules by their hydrophobic groups, especially through acyl-acyl interactions. The acyl group of emulsifiers determines its functionality in relation to TAGs. The main effects of these additives on the crystallization of fats would occur during the stages of nucleation, polymorphic transition and crystal growth, changing physical properties such as crystal size, solid fat content and microstructure. The question of promoting or inhibiting crystallization, however, is still controversial. In general, studies indicate that emulsifiers with acyl groups similar to the fat being crystallized accelerate this process (Miskandar et al. 2007).

According to Garti (2002) and Miskandar et al. (2006), the behavior of the emulsifiers during fat crystallization can be divided in three events: (1) limited miscibility between the emulsifiers molecules and TAGs: in this situation the emulsifier acts as an impurity and the interaction results in imperfect crystals, which can promote or slow the crystal growth and polymorphic transitions, according to the compatibility of the hydrophobic chains in their structures; (2) high degree of miscibility between emulsifiers and TAGs, which promotes the formation of molecular compounds; (3) total immiscibility between emulsifiers and TAGs, where emulsifiers can act as crystallization seeds and microstructural modifiers.

With regard to the polymorphic transitions, the extension of the protection provided by the emulsifiers is not yet fully known and need further studies, although the literature shows very favorable results (Hasenhuettl 2008).

The selectivity of these additives such as dynamic controllers of polymorphic transitions in fats have been explained by their ability to create hydrogen bonds with neighboring TAGs, by a process known as *Button Syndrome*, in which the presence of a specific emulsifier does not dictate the formation of a specific polymorph, but controls the degree of mobility of the molecules and their ease to undergo configuration changes. In this process, the emulsifiers can modulate the polymorphic transformations in the solid state or through the liquid state, and the temperature program controls the physical state of the crystals during the polymorphic transition and the extent of the mobility of the molecules, thus regulating the rate of polymorphic transformation (Aronhime et al. 1987).

The literature shows that, in the solid-solid transformation, the promoting or inhibiting effect of emulsifiers on the $\beta' \rightarrow \beta$ transitions are mainly dependent on the chemical structure of these compounds. This fact is particularly important when considering the $\beta^{V} \rightarrow \beta^{VI}$ transition in cocoa butter, which requires emulsifiers with high melting point, whose carbon chains must be packed with great proximity to produce a rigid structure that hinders the molecular mobility of TAGs. However, for transformations through the liquid phase, the $\beta' \rightarrow \beta$ transition is avoided by the majority of solid emulsifiers (Aronhime et al. 1988).

In particular, the more efficient emulsifiers in terms of inhibition of fat bloom have three main effects: (i) increase in the crystallization rate and reduction of crystal size; (ii) increase in the melting point of the fat base, providing greater heat resistance to the product; and (iii) prevention of polymorphic transitions (Lonchampt and Hartel 2004).

The emulsifiers with the greatest potential for controlling the crystallization of fat bases include the sorbitan esters of fatty acids, fatty esters and polyesters from saccharose, natural lecithin and chemically modified lecithin, and polyglycerol polyricinoleate (Lonchampt and Hartel 2004). In general, literature shows that these emulsifiers affect the crystallization induction times, the composition of the nucleation seeds, crystal growth rates and polymorphic transitions. However, the results are still very incomplete, because the different parameters regarding the process of crystallization have not been studied to the same extent for each one of these compounds. Besides this factor, few studies address the use of these emulsifiers in real systems and the potential synergy between them as dynamic controllers of fat crystallization under conditions of industrial processing and storage, as well as the systematic understanding of their mechanisms to optimize the use in fat bases (Weyland and Hartel 2008).

Sorbitan esters (SE)

Sorbitol is an alcohol in the hexahedral alcohols group, obtained through hydrogenation of glucose. Its free hydroxyl groups can react with fatty acids to form sorbitan esters (SE). In the production of SE, a reaction mixture containing a specific fatty acid, sorbitol and catalyst (sodium hydroxide or zinc stearate) is heated in inert atmosphere to promote simultaneous reactions of esterification and cyclization. The molar ratio sorbitol/fatty acid determines the formation of monoesters or triesters. The SE that are most well-known and used industrially include SE from lauric, palmitic, stearic and oleic acids (Hasenhuettl 2008). Figure 3 shows the chemical structure of a sorbitan monoester.

The SE are recognized for their ability to modify the crystalline morphology and consistency of fats, with effectiveness as anti-bloom agents in confectionery products containing cocoa butter and cocoa butter substitutes, highlighting the sorbitan monostearate (SMS) and the sorbitan tristearate

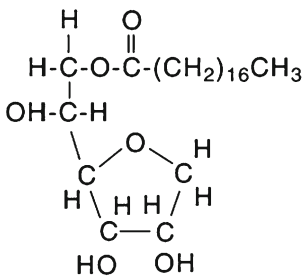

Fig. 3 Chemical structure of a sorbitan monoester. To triesters, the hydroxyl groups are esterified with fatty acids residues (R)

(STS) as potential crystallization controllers. These compounds may slow or inhibit the polymorphic transition of fat crystals more stable forms. Moreover, SE are especially effective in stabilizing the polymorph β′ in margarine and modifying the solid fat content of fats in general, to promote appropriate melting profiles at body temperature (O'Brien 2008).

The initial assessments on the effect of SE on the crystallization of lipids involved the study of pure TAGs. Aronhime et al. (1988) reported the inhibition of β-crystallization in tristearin crystallized directly from the melted state, when using SMS. According to the authors, the long hydrocarbon chain in this additive allows its solidification at temperatures close to the solidification of trisatured TAGs and its cocrystallization with them, interfering in the polymorphic transitions through steric hindrance. Sato and Kuroda (1987) investigated the incorporation of SMS and STS, at concentrations of 5 % w/w, on the crystallization properties of tripalmitin. The additives slowed the crystallization and the polymorphic transitions $\alpha \rightarrow \beta' \rightarrow \beta$.

Subsequent studies addressed the effect of emulsifiers on the crystallization of raw materials such as cocoa butter and some fat bases, such as blends for different industrial uses. Garti et al. (1986) studied the effects of SE (1–10 % w/w) on the polymorphism of cocoa butter. The authors found an increase in the $\beta^{IV} \rightarrow \beta^{V}$ transition rate, but a significant delay in the $\beta^{V} \rightarrow \beta^{VI}$ transition. Lonchampt and Hartel (2004) highlighted that the SE from palmitic and stearic acids show stabilizing effect on the intermediate form β^{V} of cocoa butter. Garbolino et al. (2005) reported that the addition of several SE (monolaurate, monopalmitate, monostearate and STS; 2 % w/w) to palm oil/interesterified palm oil and palm kernel oil/sunflower oil blends resulted in a significant modification of the crystalline morphology and consistency properties of this fat basis.

According to Weyland and Hartel (2008), STS is an additive with greater potential for the modification of cocoa butter crystallization, particularly for inhibition of the $\beta^{V} \rightarrow \beta^{VI}$ transition and fat bloom, due to its high melting point (55 °C) and chemical structure similar to TAGs from cocoa butter, allowing this emulsifier an easy cocrystallization and the formation of solid solutions with these TAGs. Berger (1990), cited by Weyland and Hartel (2008), also verified that STS showed inhibition of fat bloom and increased brightness in cake toppings based on palm kernel oil. Young and Wassel (2008) reported that the addition of 0.5 % (w/w) of STS in fat bases for margarines had a stabilizing effect on the polymorph β′. Miskandar et al. (2006) observed that aggregates of small crystals were formed in palm oil/palm kernel olein blends when adding 0.09 % (w/w) of STS, in addition to increasing the crystallization rate of these mixtures. Pernetti et al. (2007) emphasized that the use of STS and/or its combination with other emulsifiers is the most important alternative for the control of polymorphic transitions and structuring crystal fat networks, as the TAGs-STS interaction promotes the formation of regular crystals with melting point around 40 °C, characteristic of many fat bases used in industrial applications.

In order to evaluate the effect of different sorbitan monoesters as crystallization modifiers, the components sorbitan monolaurate, monopalmitate, monostearate and monooleate were added to cocoa butter at concentrations of 0.5, 1.0 and 1.5 % (w/w) (Masuchi et al. 2012). Table 2 presents the solid content according to AOCS official method (2009) for pure cocoa butter, pure emulsifiers and their blends, evaluated through Nuclear Magnetic Resonance (NMR). An increase in the solid fat content was noted, mainly at the temperatures of 10 and 15 °C, for samples containing cocoa butter with sorbitan monostearate and monopalmitate at the different concentrations, but with greater increase in solid fat content for samples containing 1.5 % of these emulsifiers.

Figure 4 presents the crystallization events by differential scanning calorimetry (DSC) for pure cocoa butter, cocoa butter samples with 1.5 % of sorbitan monostearate (CB SMSt 1.5 %) and 1.5 % of sorbitan monopalmitate. The samples CB SMSt 1.5 and CB SMP 1.5 % showed variations in the onset crystallization temperature of 4.7 and 3.6 °C, respectively, compared to pure cocoa butter. Thus, the addition of these emulsifiers induces crystallization of cocoa butter, anticipating the solidification process.

Sucrose esters of fatty acids (SEFAs)

Sucrose esters of fatty acids (SEFAs) are mono-, di- and triesters of sucrose with food fatty acids, prepared from sucrose and methyl and ethyl esters of food fatty acids or by extraction from sucroglycerides (Hasenhuettl 2008). SEFAs are extremely functional emulsifiers, as they are characterized by unique advantages to the food industry. They are nontoxic compounds, tasteless and flavorless, easily digested, as well as biodegradable under aerobic and anaerobic conditions. The SEFAs are produced by interesterification between sucrose and fatty acids through different reaction mechanisms. They have typical structure of polar and nonpolar groups in the same molecule like other emulsifiers, but the eight possible positions for esterification with fatty acids allow different lipophilic/hydrophilic properties for these molecules. The partially esterified SEFAs, mainly the mono-, di- and triesters, are the most versatile components for use in food, and their esterification degree is controlled by the fatty acids/sucrose ratio in the reaction system. The degree of saturation and the size of the fatty acid chain also significantly influence the properties of these compounds. Sucrose fatty polyesters (SFPs) are synthesized with a high degree of substitution (six to eight groups per molecule), usually from a interesterification reaction in two stages (Garti 2002; Hasenhuettl 2008). Figure 5 shows the chemical structure of a sucrose fatty diester.

Table 2 Solid fat content (SFC), in %, of pure cocoa butter (CB), pure sorbitan monoesters: monolaurate (SMLa), monopalmitate (SMP), monostearate (SMSt) and monooleate (SMO), and cocoa butter added with 0.5, 1.0 and 1.5 % (w/w) of each emulsifier

	Temperature (°C)							
Sample	10	15	20	25	30	35	45	65
CB	76.4	71.9	65.5	54.8	27.9	0.6	–	–
SMLa	43.0	21.5	4.5	2.3	1.6	0.9	–	–
CB SMLa 0.5 %	78.6	72.4	65.1	54.1	25.8	0.2	–	–
CB SMLa 1.0 %	78.2	72.3	65.9	53.2	25.8	0.4	–	–
CB SMLa 1.5 %	76.3	72.1	65.0	53.5	25.8	0.6	–	–
SMP	92.3	90.8	89.1	87.7	85.9	82.4	49.1	0.4
CB SMP 0.5 %	79.6	72.9	66.6	54.6	26.5	0.3	–	–
CB SMP 1.0 %	79.9	73.4	66.8	54.5	25.6	0.7	–	–
CB SMP 1.5 %	79.3	74.8	67.3	55.1	25.9	0.8	–	–
SMSt	96.4	95.3	94.1	93.1	92.1	90.4	72.0	0.5
CB SMSt 0.5 %	79.4	73.2	67.0	54.9	27.1	0.4	–	–
CB SMSt 1.0 %	80.3	73.3	66.2	54.0	27.7	0.6	–	–
CB SMSt 1.5 %	81.4	74.7	68.0	55.9	29.1	0.6	–	–
SMO	2.9	1.9	1.3	0.8	0.6	0.0	–	–
CB SMO 0.5 %	77.5	70.9	65.4	53.3	27.2	0.7	–	–
CB SMO 1.0 %	76.7	70.9	65.2	53.2	26.6	0.6	–	–
CB SMO 1.5 %	76.3	70.9	64.1	53.2	25.6	0.5	–	–

In spite of its great versatility of use in food products, including applications such as synthetic fat replacers, studies on the use of SEFAs as crystallization modifiers in fats are recent, but have great potential,, especially when considering issues of adequacy of fats for industrial use. Few works have explored the effect of these emulsifiers on the induction period and crystallization rate and the development of polymorphic forms in fat systems. Regarding the use of SFPs, studies are even more scarce (Cerdeira et al. 2006). According to Lonchampt and Hartel (2004), these additives should also be evaluated as inhibitors or retardants of fat bloom in chocolate and similar products. Oh et al. (2005) consider that these emulsifiers can improve the quality and stability of foods with the desirable polymorph β′.

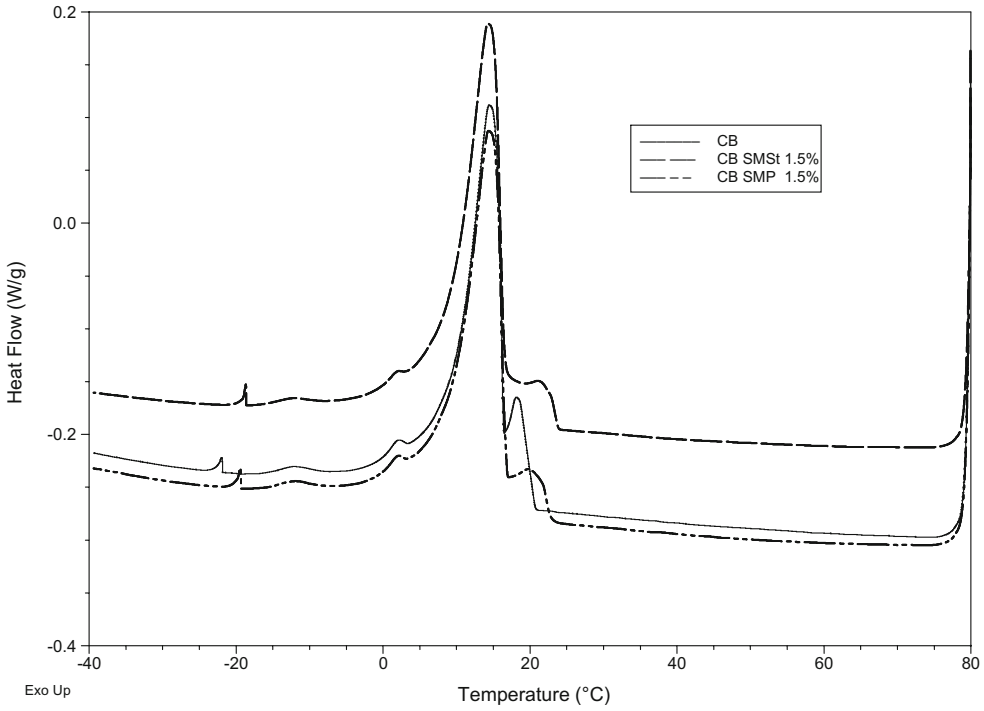

Fig. 4 Crystallization curves obtained by Differential Scanning Calorimetry for pure cocoa butter (CB) and samples of cocoa butter added with 1.5 % (w/w) of sorbitan monostearate (CB SMSt 1.5 %) and 1.5 % (w/w) of sorbitan monopalmitate (CB SMP 1.5 %)

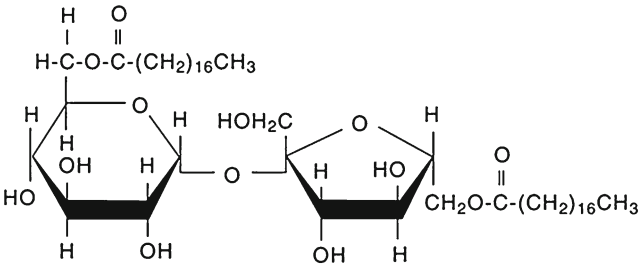

Fig. 5 Chemical structure of a sucrose fatty diester. For polyesters, the hydroxyl groups are esterified with residues fatty acids (R)

In studies with pure TAGs, Elisabettini et al. (1996) reported that the addition of 5 % of sucrose monostearate to tristearin (SSS) efficiently slowed the $\alpha \rightarrow \beta$ and $\beta' \rightarrow \beta$ transitions. Moreover, Oh et al. (2005) found that the polymorphic transitions of tristearin in the presence of SFP were dependent on the molecular structure of these compounds, especially with respect to the chain size and the degree of substitution of fatty acids.

Some studies show the effect of the incorporation of SEFAs in fat blends. Yuki et al. (1990), cited by Martini et al. (2004), studied the crystallization behavior of blends of 60 % partially hydrogenated soybean oil/30 palm oil/10 % canola oil, with incorporation of 0.5 % (w/w) of different SEFAs. The SEFAs from palmitic and stearic acids accelerated the crystallization, while the SEFA from lauric acid slowed this process. Nasir (2003) verified that the addition of sucrose tetrastearate (1.0 % w/w) to the blend consisting of 90 % partially hydrogenated soybean oil /10 % cottonseed oil produced an increase in the crystallization rate and solid fat content of this basis. According to the author, the use of SEFAs in fats can reduce the time of conventional tempering in several applications in the food industry. Cerdeira et al. (2003) evaluated changes in the properties of crystallization of sunflower oil/fat blend, from the use of different SEFAs, at the concentrations of 0.1 and 0.5 % (w/w). According to this study, these components slowed the nucleation processes of samples. Particularly, the SEFAs from palmitic and stearic acids showed a significant effect in decreasing the crystal sizes and in the modification of crystalline distribution, positively associated with changes in fat bases with large crystals, such as blends of hardfats and liquid oils. In a later study with the same raw materials and additives, Cerdeira et al. (2006) observed that, under static crystallization, the additives favored the formation of the β' polymorph and slowed the formation of the β polymorph; in dynamic crystallization conditions, action of the additives resulted in a decrease of the crystal sizes, but showed no effect on the crystalline morphology.

In the only study found in literature using cocoa butter added of SEFAs from lauric, myristic, palmitic, stearic and oleic acids, at the concentration of 5 % w/w, Oh and Swanson (2006) observed that the addition of emulsifiers to cocoa butter changed the rate of the $\beta^{V} \rightarrow \beta^{VI}$ transitions, and this effect depends on the fatty acid composition of the emulsifier. The SEFAs containing fatty acids of similar size to the fatty acids predominant in cocoa butter fully inhibited this transition.

Lecithin

In general usage, lecithin refers to a complex, naturally occurring mixture of phospholipids, lipids containing a phosphoric acid residue; they are nature's principal surface-active agents. They are found in all living cells, whether of animal or plant origin. Lecithin is obtained by water-degumming crude vegetable oils and separating and drying the hydrated gums. It is, however, the phospholipid portion of lecithin that is mainly responsible for giving form and function to commercial lecithin (Szuhaj 2005).

Lecithin is the emulsifier with higher functionality for use in the food industry. Commercially, soybean oil is the main source of this additive. Food-grade standard lecithin is a complex mixture of phosphatides, which contains mainly phosphatidylcholine (12–18 %), phosphatidylethanolamine (10–15 %), phosphatidylinositol (8–11 %) and phosphatidic acid (3–8 %), combined with other substances, such as TAGs, free fatty acids and carbohydrates (Fig. 6). According to the oil content, lecithin can be classified as liquid, plastic or semi-solid, in which the percentages of phospholipids vary between 60 and 65 %; in the oil free form, lecithin presents phospholipids levels higher than 90 % (O'Brien 2008). Further, standard lecithin can be modified, giving rise to compounded lecithin (combined with other surfactants or additives), fractionated lecithins and chemically modified lecithins (hydrogenated, hydroxylated, halogenated, sulfonated and acetylated). In this last group, the hydroxylated and acetylated lecithins stand out as the species with greater functionality (Garti 2002).

Lecithin is the most widely used additive in confectionery fats and chocolates. As its sensory properties are very similar to those of fats, the use of lecithin enables the reduction of fat levels in many formulations. In chocolates, the use of lecithin reduced viscosity, improved snap and resistance to fat bloom and temperature variations. For example, the addition of 0.5 % of lecithin in a chocolate coating provides reduction in

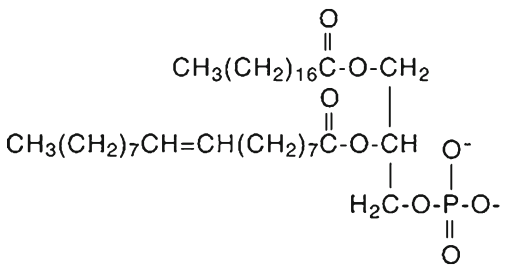

Fig. 6 Chemical structure of phosphatidylcholine

viscosity similar to the addition of 5 % of cocoa butter or vegetable oil (Timms 2003).

As a result of their pronounced amphiphilic characteristics, natural or modified lecithins have drawn attention as modifiers agents of fat crystallization processes, especially regarding the nucleation process and microstructure. Although lecithin is present in many fat matrices, such as margarine and chocolate, its functional use as an active agent in the microstructural and kinetic modifications of fats was evaluated only in a few studies, and just recently the studies were directed to the cocrystallization events and structural modification associated with the use of this emulsifier (Pernetti et al. 2007). Different kinds and concentrations of lecithin and their combinations with other additives in a fat system can display very different effects with regard to the changes in the crystallization rate and crystal morphology, in addition to reducing viscosity and consistency. Thus, the understanding of the mechanisms related to these changes is essential so that the use of this emulsifier can be optimized as an effective controller of crystallization in fat bases for different foodstuffs (Weyland and Hartel 2008).

The influence of incorporating lecithin in chocolate was recently the subject of study of Afoakwa et al. (2008). The authors evaluated the addition of two different levels (0.3 and 0.5 % w/w) of standard lecithin to dark chocolate. The incorporation of lecithin influenced the degree of crystallinity and the melting events of the chocolate mass; the increased lecithin content reduced the size of the crystals and decreased the values of final temperature, peak temperature and melting enthalpy. According to this study, the amphiphilic nature of lecithin would be responsible for crystal deagglomeration, with effects on the physical properties. The authors also highlight that the knowledge on the influence of the type and content of lecithin would have important applications in defining the quality of chocolates, with respect to the characteristics of morphology and dimensions of crystals and polymorphic stability.

In studies on the processes of fats post-crystallization, Johanson and Bergenstahl (1995) reported that lecithin avoided the sintering phenomenon in soybean oil/palm stearin/fully hydrogenated palm kernel oil/partially hydrogenated canola oil blends. This effect was later proven by Harada and Yokomizo (2000), who verified that lecithin adsorb in crystalline interfaces, slowing or even inhibiting the process of sintering in fats during storage.

Regarding to the influence of lecithin on the crystallization kinetics and crystalline microstructure, studies are scarce in literature. Evaluations made by Dhonsi and Stapley (2006) suggested that the addition of 0.2 % of standard lecithin to cocoa butter slightly increased the induction period of crystallization. Miskandar et al. (2006, 2007) observed that 0.03 % lecithin content promoted the formation of small and homogeneous crystals in palm olein/palm oil blends and accelerated the crystallization of the samples. In contrast, the incorporation of lecithin at the levels of 0.06 and 0.09 % inhibited the crystallization of these mixtures.

In spite of its large availability and industrial use, there is a wide gap of knowledge on the accurate effect of the use of lecithin as a crystallization modifier in fats. The available results indicate the formation of more homogeneous crystalline networks, decreased size of crystals and increased induction period, as well as post-processing stability. However, no precise information is available on the percentages of this emulsifier favorable to the processes of crystallization in relation to specific fats. Farther, studies on the functions of chemically modified lecithins on the crystallization of fat bases are still unknown, but have great potential according to the diversification of the functional groups in the molecules of these additives (Pernetti et al. 2007; Weyland and Hartel 2008).

Miyasaki et al. (2012) studied the influence of modified soybean lecithin (acetylated, hydroxylated, enzymatically hydrolyzed and deoiled) on the process of crystallization of cocoa butter in different concentrations (0.2, 0.5 and 0.8 % w/w). The results were compared with the data obtained using standard lecithin. The TAG composition of the cocoa butter was 19.89 % for POP, 39.74 % for SOS and 21.60 % for POS and the amounts of trisaturated, mono-, di- and tri-unsaturated TAGs were 1.55, 87.70, 9.99 and 0.76 %, respectively. In all samples tested, the average values of solid fat content did not show differences and were approximately 76 % (10 °C), 70 % (15 °C), 63 % (20 °C), 53 % (25 °C), 27 % (30 °C), 0.5 % (35 °C) and 0.3 % (40 °C). The curves showed a typical sigmoidal shape of crystallization isotherms of cocoa butter. The addition of modified lecithins in different concentrations changed the induction time and the Avrami parameters. In relation to the samples with concentrations of 0.2 % of emulsifier, they showed an effect that was more pronounced or similar to those with a concentration of 0.5 % in relation to the crystallization rate. In Fig. 7, we present the isotherms of the samples of CB+ lecithins at the concentration of 0.2 %, obtained by Nuclear Magnetic Resonance (NRM). The equilibrium in the solid fat content (SFC (∞)) was reached for all samples in approximately 110 min. The behavior of the samples containing 0.5 % of emulsifier was similar to those with 0.2 %, whereas samples with 0.8 % presented curves that approached those of cocoa butter without emulsifier. Additionally, we can observe two regions where there is a visible distinction of the effect of emulsifiers. One refers to the nucleation onset and crystal growth, in the period between 10 and 12 min, and the other refers to the period of intense crystalline growth, between 35 and 80 min. In the latter region, a discrepancy can be seen in terms of CGS of samples with added emulsifier and pure cocoa butter. The Avrami parameter n was obtained from the data of isothermal crystallization at 15 °C and was approximately 2, suggesting

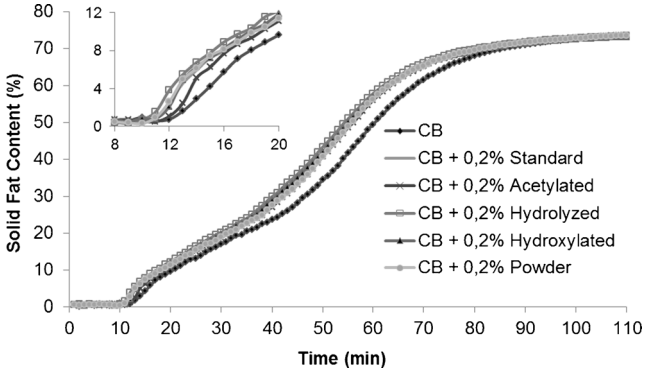

Fig. 7 Crystallization Isotherm of pure cocoa butter sample and cocoa butter with different added lecithins (concentration of 0.2 %) at 15 °C, obtained by nuclear magnetic resonance

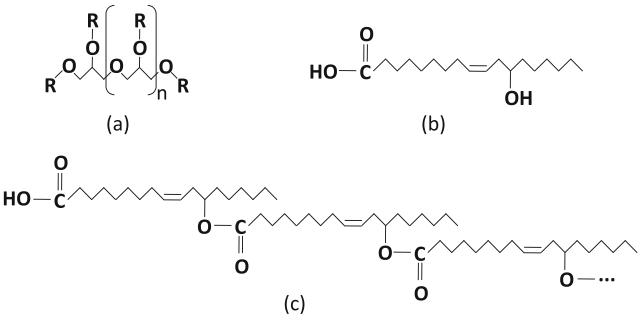

Fig. 8 Chemical structure of polyglycerol polyricinoleate (PGPR)

uniformity of the crystal types formed and growth mechanisms. Samples with 0.2 % of emulsifier enabled a better differentiation between effects. Among the emulsifiers tested, the enzymatically hydrolyzed lecithin was the most effective in accelerating the crystallization, followed by standard, hydroxylated, deoiled and acetylated lecithin, in that order. The values of the Avrami parameters, *n* and *k*, for samples with emulsifier concentration of 0.2 %, were: 2.10 and 2.80 E-04; 2.16 and 2.12 E-04; 2.16 and 2.12 E-04; 2.15 and 2.13 E-04; 2.28 and 1.29 E-04, respectively. Pure cocoa butter presented values of *n* and *k* equal to 2.34 and 8.42 E-05, respectively. Based on these results, enzymatically hydrolyzed lecithin demonstrates great potential to be used in the production of chocolate and other confectionery applications.

Polyglycerol polyricinoleate (PGPR)

Polyglycerol polyricinoleate (PGPR) consists of polyglycerol esters of interesterified fatty acids present in castor oil. It is insoluble in water and ethanol and soluble in ether (Hasenhuettl 2008). Polyglycerol esters are formed by the reaction of fatty acids with glycerol, containing polymers with 2 to 10 molecules. The production of these emulsifiers includes polymerization and esterification processes, which must be carefully controlled in order to obtain specific properties. They are multifunctional additives, property that allows their use as emulsifiers or fat substitutes (O'Brien 2008).

PGPR is one of the more hydrophobic emulsifiers used in foods. This additive has gained attention recently because of its approval for use in confectionery fats, notably in chocolate-based products. The obtaining of PGPR consists of three phases: polymerization of glycerol at elevated temperatures, forming of polycondensated ricinoleic acid and esterification between polyricinoleic acid and polyglycerol at mild temperatures for the formation of oligomers (Garti 2002). Its chemical structure is shown in Fig. 8.

The functionality of PGPR in chocolate has been linked mainly to the reduction of consistency (or yield value), with limited effect on viscosity. Its synergistic effect with lecithin has recently been documented, but the specific mechanisms of action have not yet been fully clarified. Weyland and Hartel (2008) state that the use of PGPR associated with lecithin is the best alternative for viscosity modification in coatings and chocolates, allowing significant adjustments in the levels of cocoa butter or vegetable fat in a particular formulation, with significant reduction of costs. Schantz and Rohm (2005) point out that the optimization of the use of these additives combined in chocolates and similar products would allow the development of innovative products such as thin coatings with high stability.

Rousseau et al. (2005) showed that the polymorphic form and crystalline morphology of the canola oil/4 % fully hydrogenated cottonseed oil blend can be manipulated through the use of PGPR (0.125 % w/w) under different tempering conditions. The presence of PGPR in the concentration evaluated altered the crystal habit and the morphology of the blends, in stirred (240 rpm) crystallization at 5 °C, with a significant increase in the proportion of form β′. The authors suggest that PGPR could produce changes in short spacings that are characteristic of a fat, with the combined use of stirring (factor responsible for the incorporation of PGPR in the inclusions of crystalline forms), thus significantly slowing the $\alpha \rightarrow \beta' \rightarrow \beta$ transitions.

Stroppa et al. (2011) evaluated the impact of the use of lecithin and PGPR on the rheological characteristics (Casson model), temper index, snap of chocolate bars and crystallization kinetics through a simulation of the conventional process of chocolate production: tempering with optimized conditions of time and temperature, but statically, and a subsequent isothermal cooling to complement the crystallization. Expected effects of reduction of plastic viscosity and yield limit were found. The authors highlight that the use of PGPR could introduce beneficial effects on the crystallization of fats, through easier and faster tempering processes, microstructural modifications and possible prevention of fat bloom. However, the contribution of PGPR as controller or modifier of crystallization and polymorphism in fat systems is almost unknown and has become the subject of interest to food technology. Fundamental studies are still needed to explain the reactivity

of this emulsifier in the processes of crystallization, primarily in relation to cocoa butter (Garti 2002; Lonchampt and Hartel 2004).

Conclusions

This study conducted a comprehensive review of the effects of several compounds as crystallization modifiers of lipid phases, to provide input to the knowledge on the crystallographic, microstructural and kinetic phenomena involved in the processes for modifying the crystallization of fats and oils. Minor lipids, specific TAGs, in addition to a series of emulsifiers, employed at low concentrations, proven effective agents in the processes of lipid modification, representing a highly viable option, in economic terms, for modulating the crystallization properties of industrial oils and fats.

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