Conventional and non-conventional lipid modifications: a review

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Conventional lipid modification processes are able to redesign oils and fats depending on the desired functionality profile and the intrinsic characteristics of the raw materials by chemical modification of the fatty acids (hydrogenation); by reversing the ester linkage (hydrolysis); by physically separating triacylglycerols from glycerol with distinct melting points (fractionation) and rearrangement of fatty acids in the triacylglycerols main chain (interesterification). Although these processes are technologically functional, the substitution of fats in food products is a challenge because is difficult to obtain the satisfactory characteristics when there is no trans fatty acids and with reduction of saturated fatty acids. Thus, organogels technology appears with a new range of lipid structures capable of forming a three-dimensional network that immobilizes liquid oil, resulting in lipid bases with distinct macroscopic characteristics, rich in unsaturated fatty acids that shows potential for substitution of the technical fats obtained by the conventional processes of lipid modification, aiming at industrial products of better nutritional profile.

Keywords: Lipid modification; Organogel; Structuring lipids

1. Introduction

The imbalance in lipoprotein metabolism caused by dietary habits with high intakes of saturated and trans fats and cholesterol causes increased concentration of total cholesterol and low density lipoprotein (LDL), reducing the fractions of high density lipoprotein (HDL), affecting the LDL/HDL ratio, which favors the onset of cardiovascular diseases. Conventional lipid modification processes are able to redesign oils and fats depending on the desired functionality profile and the intrinsic characteristics of the raw materials by chemical modification of the fatty acids (hydrogenation); by reversing the ester linkage (hydrolysis); by physically separating triacylglycerols (TAG) from glycerol with distinct melting points (fractionation) and rearrangement of fatty acids in the TAG main chain (interesterification). Although these processes are technologically functional, the substitution of fats in food products is a challenge, since technologically satisfactory crystallization and consistency properties are difficult to obtain when there is no trans fatty acids and reduction of saturated fatty acids. As a consequence, public policies that directed the food industry to change the lipid raw materials conventionally employed, aiming for greater consumer health, were implemented. Thus, the technology of organogels appears with a new range of lipid structures capable of forming a three-dimensional network that immobilizes liquid oil, resulting in lipid bases with distinct macroscopic characteristics and obtained with raw materials free of trans fatty acids and rich in unsaturated fatty acids. Organogels, viscoelastic materials composed of structuring agents and an apolar liquid phase, show the potential for substitution of the technical fats obtained by the conventional processes of lipid modification, aiming at industrial products of better nutritional profile.

2. Lipids

The term lipid is derived from the Greek *lipos*, which means fat. However, a number of compounds can be accommodated in this group: oils (mixtures of TAGs in liquid form at room temperature), fats (TAG blends in solid form at room temperature), waxes (esters formed by fatty acids with long-chained alcohols), as well as soaps, steroids, detergents and bile salts [1].

Lipid-forming fatty acids are hydrocarbon derivatives and have a very low oxidation state, similar to the hydrocarbons present in fossil fuels, which means that fatty acids are highly reduced. In addition, they may have chains of 4 to 36 carbons, saturated or unsaturated. Frequently occurring fatty acids in nature have even numbers of carbon atoms in an unbranched chain containing from 12 to 24 carbons. Likewise, in the unsaturated fatty acids, the double bond is generally located at carbons 9 and 10 and are separated by methylene groups, that is, for the most part, unconjugated double bonds occur [2].

According to the primordial chemical structure of lipids, these can be classified as acylglycerols, which have fatty acids esterified to a glycerol molecule. The number of esterified fatty acids classifies acylglycerol in monoacylglycerol (one esterified fatty acid), diacylglycerol (two esterified fatty acids) and TAG (three esterified fatty acids). Natural fats, such as vegetable oils and animal fat, correspond to complex mixtures of simple and mixed TAGs containing a variety of fatty acids that differ in chain length and degree of saturation [2].

From a dietary and nutritional point of view, edible oils and fats are essential nutrients in the human diet, playing a vital role through the delivery of essential fatty acids and energy. In addition to the nutritional qualities, oils and fats provide consistency and melting characteristics specific to the products that contain them as well as acting as a mean of heat transfer during the frying process and as carriers of fat-soluble vitamins and aroma [3].

3. Saturated fats

All humans need a lipid source in their diet. However, the increasing incidence of cardiovascular diseases in the last century has led to a great search for the risk factors related to its development. Thus, several studies have found that the relatively high intake of saturated fat (approximately 17% of total energy) is an important contributor to the high incidence of coronary heart disease [4]. Unbalance in lipoprotein metabolism and dietary habits are major risk factors for cardiovascular diseases. Western diets, with high concentrations of saturated fats and cholesterol, increase the concentration of total cholesterol and low-density lipoprotein (LDL). The activity of the hepatic LDL receptor is generally the main factor controlling plasma LDL, dietary cholesterol and saturated fats, since they suppress this receptor by increasing plasma cholesterol concentrations[1,5].

Saturated fatty acids are naturally present in oils and fats of plant and animal origin, and may produce interesterified or fractionated fats [6,7]. However, when this saturated fat is replaced by a source rich in polyunsaturated fatty acids, a reduction in the plasma cholesterol concentration associated with LDL also occurs, as well as anti-inflammatory actions on the vascular cells, since these fatty acids inhibit the expression of proinflammatory endothelial proteins [4,8].

4. Trans fats

The trans fatty acids (TFA) are geometric and positional isomers of natural unsaturated fatty acids. In this configuration, two hydrogen atoms attached to the carbon atoms forming the double bond are located on opposite sides of the carbon chain, forming a linear and more rigid molecule. Because of their structural characteristics, trans fatty acids have a higher melting point than when compared with their corresponding *cis* isomer [9].

TFAs are naturally present in fats from ruminant animals as a result of the biohydrogenation process in the microbial flora of the rumen. However, TFAs also originate from partial catalytic hydrogenation of vegetable or marine oils. About 90% of TFA in food derives from this process. Hydrogenation is carried out with the aim of modifying the composition, structure and consistency of an oil. This results in the reduction of the degree of oil unsaturation and increase of its melting point, associated with the increase in the oxidative stability and functionality of the semisolid fractions produced [10].

The TFAs are included among dietary lipids that act as risk factors for coronary artery disease, modulating the synthesis of cholesterol and its fractions and acting on eicosanoids. Several studies have suggested a direct relationship between TFA and increased risk of vascular diseases [5,10–12]. The excess of TFA, from the biological point of view, favors the production of eicosanoids without biological activity, since it has priority of desaturases enzymes [1]. In contrast to all other fatty acids, the trans isomers imply a decrease in high-density lipoprotein (HDL) and an increase in LDL cholesterol, affecting the LDL/HDL ratio unfavorably compared with the modification caused only by saturated fatty acids [13].

5. Regulatory aspects

Due to the harmful effects of TFAs and saturated health, several actions have taken place from both Health Regulatory Agencies and Societies responsible for the elaboration of Nutrition Guidelines, in order to recommend the reduction of consumption of these fatty acids by the world population. Thus, public policies that directed the food industry to change the lipid raw materials conventionally employed, aiming for greater consumer health, were implemented [8].

Regarding international bodies, the Food and Drug Administration (FDA) requires that trans fats be declared in the nutritional information on the label of industrialized products since 2006. Recently, in June 2015, a new resolution called for the complete removal of trans fats in processed foods. This measure was taken aiming to reduce the incidence of cardiovascular disease and prevent thousands of fatal heart attacks that occur every year in the United States of America. In addition, the TFAs were also excluded from the GRAS ("generally recognized as safe") classification food safety indicator for human consumption [14].

As a precautionary measure, the FDA has also developed consumer guidelines recommending the choice of non-fat trans and reduced in saturated fat food products. The recommendation also warns about the minimum levels of TFA, since products with contents less than 0.5g of TFA in the portion do not have this component declared in the nutritional information. Therefore, it is recommended to check the listing of ingredients and if there is presence of partially hydrogenated fat, rich in TFA [14].

In Europe, however, the body responsible for food regulations is the European Food Safety Authority, which has warned about the increased risk of death from cardiovascular disease when daily intake of TFA exceeds 2% of total energy value. However, Europe does not have standard legislations for the whole continent – each country has the authority to set limits and recommendations. Possible approaches for European countries to limit the levels of TFA in food can be divided into legislative actions and voluntary measures. Legislative actions define limits (either at the level of ingredients or in the final product) or recommendations on the consumption of TFA in nutritional information and was adopted by Austria, Denmark, Latvia and Hungary. In other countries, there is voluntary inclusion of the trans fat

content in nutrition information, with Belgium, Denmark, the Netherlands, Poland, the United Kingdom and Greece are making their own regulations; While Bulgaria, Malta, Slovakia, the United Kingdom and Finland included dietary recommendations and Estonia changed the criteria for producing food products. Studies have noted that legislative actions were more effective in eliminating TFA in food than voluntary measures [15].

From these considerations, the field of knowledge in lipid technology has sought alternatives to reduce the amount of saturated and trans fats in foods, as well as reducing the caloric intake associated with the lipid content in processed products.

6. Lipid modification processes

Most natural oils and fats have limited application in their unaltered forms, imposed by their particular composition in fatty acids and TAGs. However, in the last decades there has been an increasing interest in the technology of modification of oils and fats. This trend can be attributed mainly to the fact that these materials are obtained from natural sources and are used as important raw materials for the food, chemical and pharmaceutical industries. Therefore, the industrial sector of oils and fats has developed several processes to alter the composition of TAG mixtures [16].

6.1 Conventional processes

In conventional lipid modification processes the basic structure of oils and fats can be redesigned depending on the desired functionality profile and the intrinsic characteristics of the raw materials by chemical modification of the fatty acids (hydrogenation); by reversing the ester linkage (hydrolysis), by physical separation of phases of fatty acids (TAG) from glycerol with distinct melting points (fractionation) and rearrangement of fatty acids in the TAG main chain (interesterification) [3].

Hydrogenation is a process of modification of oils aimed at obtaining fatty bases for the formulation of several food products. Partial hydrogenation modifies the plasticity of the lipid base and generates trans fatty acids. The reaction occurs at the active sites of the catalyst, usually nickel, where the gaseous hydrogen comes in contact with the double bonds of the unsaturated fatty acids present in the oil or fat, giving rise to saturation or isomerization reactions. The double bonds can be repositioned (position isomerization) or modified from the *cis* configuration to a thermodynamically more stable form, by the trans-isomerization mechanism [16]. In turn, total hydrogenation promotes the saturation of all the double bonds of the fatty acids of the starting raw material without forming trans isomers [17].

Interesterification is a process of modification of oils and fats that promotes a redistribution of fatty acids in the chains of glycerol. The reaction begins when the catalyst is added to the oil or fat, promoting the cleavage of the TAG ester bonds. The fatty acids in the free form are re-esterified intra- or intermolecularly, usually resulting in products with distinct melting and crystallization characteristics of the original raw materials [18]. Although interesterified fats are free from trans isomers, fatty acid distribution may occur at the 1, 2 and 3 positions of the glycerol molecule, whose alterations may induce an increased risk of developing cardiovascular diseases [5].

Data from the literature show controversial results regarding the action of these fats on the lipid profile, since different types of fatty acids can be used in their formulation. Thus, it is necessary that studies evaluate not only the action of the various saturated fatty acids used, but also the possible metabolic implications resulting from the modification of the position of these fatty acids in the glycerol molecule [8].

The fractionation process, in turn, consists of the thermomechanical separation in two steps: partial crystallization in liquid phase and filtration. In the first step, the molten fat is cooled and maintained at the desired crystallization temperature until partial crystallization of the higher melting point TAG occurs. At the end of the crystallization step, the two phases are separated by filtration to give stearin (solid phase) and olein (liquid phase). The stearin consist of TAGs rich in saturated fatty acids, SSS (saturated saturated-saturated) and SSU (saturated-saturated-unsaturated) types, while olein is TAG-rich UUU (unsaturated-unsaturated) and UUS (unsaturated unsaturated) [3].

Fractionation and the use of *blends*, that is, mixtures of fats with different physical properties, represent alternatives for obtaining fatty bases with physical properties and plasticity suitable for use in several products, although with limited potential by the chemical composition of the raw materials themselves [19].

Although the processes of interesterification, fractionation and mixing are very technologically functional, the substitution of partially hydrogenated or interesterified fats in food products is currently a challenge, since appropriate characteristics of crystallization and consistency are difficult to obtain when there is absence of trans fatty acids and saturated fatty acids [20].

6.2 Lipids structuration

In recent years, interest in the influence of specific additives or minor components in oils and fats on the physical properties of fatty systems has significantly increased [21]. Modification of physical properties of lipid matrices has been a strategic subject for the processing of high-fat foods, aiming at product suitability, cost reduction, quality improvement and increased applicability and stability of different lipid raw materials [21–23]. Different materials have

been evaluated, such as trisaturated TAGs, free fatty acids, partial acylglycerols (monoacylglycerols and diacylglycerols), phospholipids, phytosterols and emulsifiers [24].

Generally, the structuring of oils and fats is carried out through the organization of the TAG in the initial stages of the solidification process forming a network of small crystals in the oil. The size and shape of these crystals can be controlled by the shear rate and degree of cooling, determining the mechanical properties of the crystalline lattice [25].

The range of publications available to date indicates that the various components, either natural or added to the lipid matrix, act at the molecular or sub-micron level on the overall structuring process, involving nucleation, crystalline growth, morphology, thermal behavior and polymorphic stability. Similarly, the effects of these modifiers at the macroscopic level, such as visual appearance, melting profiles, rheology and consistency, have also been the subject of further studies [24].
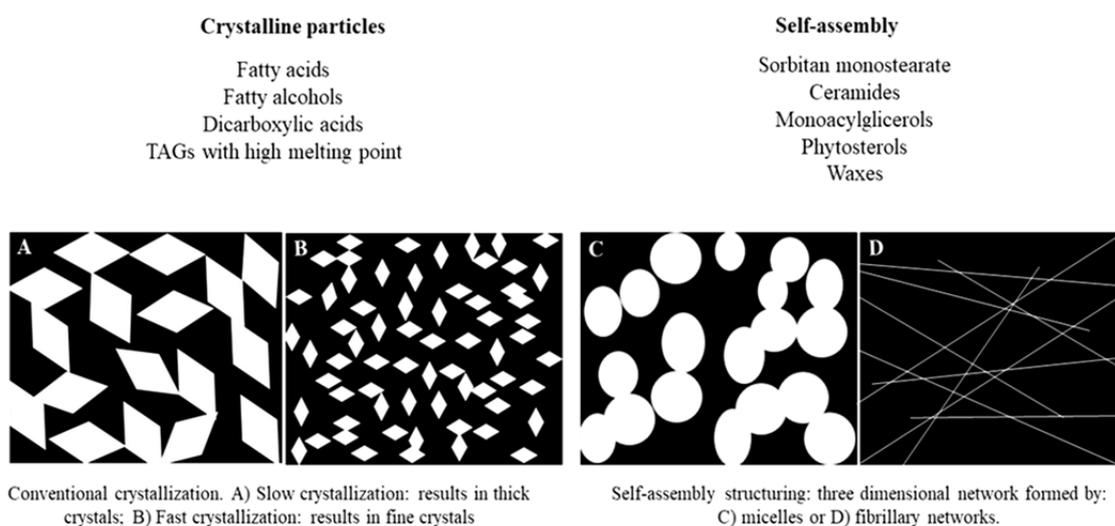
In this context, in addition to the conventional structuring of TAG, studies on a new range of lipid structures have shown several effective compounds for the formation of a three-dimensional network able to immobilize the liquid oil, forming lipid bases with distinct macroscopic characteristics as an alternative to the conventional structuring agents rich in saturated fatty acids or trans fatty acids. Products of this new technology have been denominated organogels or oleogels [26].

7. Organogels theory

By definition, organogels are semi-solid systems, where the oil phase is immobilized by a self-sustaining three-dimensional network formed by the structuring agents [22,24–27].

The organogel-forming structuring agents are characterized as lipid materials capable of capturing a large amount of liquid oil, and can be classified into two groups: self-assembling systems (self-assembly) or crystalline particle systems. Both structuring agents act as building blocks forming three-dimensional networks in liquid or semi-solid oils. The size of the structuring agents and their interactions may determine the final structure of the product and its characteristics (Figure 1) [25,27]. The structuring can be achieved by dispersing the structuring agents in the continuous phase. These structuring agents may be macromolecules, such as proteins or polymers, or low molecular weight compounds such as fatty acids, fatty alcohols or TAGs. The interaction between them can be of different natures through covalent bonds, electrostatic forces, hydrogen bridges or Van der Waals forces. Generally, a small amount of structuring interacting with the continuous phase is sufficient for forming a network [25].

Structuring mechanisms

Crystalline particles

Fatty acids
Fatty alcohols
Dicarboxylic acids
TAGs with high melting point

Self-assembly

Sorbitan monostearate
Ceramides
Monoacylglicerols
Phytosterols
Waxes

Conventional crystallization. A) Slow crystallization: results in thick crystals; B) Fast crystallization: results in fine crystals

Self-assembly structuring: three dimensional network formed by: C) micelles or D) fibrillary networks.

Fig. 1 Different structuring mechanisms obtained in organogels.

The structuring agents of the crystalline particles type form colloidal crystalline lattices inducing the crystallization of the TAGs, which when subjected to cooling, limit the solubility of the higher melting molecules leading to the nucleation events. In this system, the crystals grow and interact with each other through non-covalent forces forming a continuous three-dimensional network. After completion of the crystallization, the crystals aggregate forming larger and larger agglomerates from weak bonds, and give rise to the final macroscopic characteristics [25].

The self-sustaining promoter structures may be represented by macromolecules, low molecular weight compounds such as fatty acids and fatty alcohols, mixtures of phytosterols-oryzanols, sorbitan monostearate, sorbitan tristearate, mixtures of lecithin and waxes. Using these agents, liquid or semi-solid vegetable oils can be structured as gels, forming

continuous networks, micelles or fibrillary networks from aggregates of micelles, developing inverse bilayer structures in the form of rods, characterizing the materials recognized as organogels or oleogels [21,25].

When the structuring agents used are of lipid origin, the formation of the gels occurs through an extension of the conventional crystallization process, the type, morphology and mode of growth of the crystals being distinct from the conventional crystallization mode, resulting in networks through the oil-structuring bonding capacity [28].

In gels added with only one component, as in the case of waxes in oil, this structuring intensifies linearly to the length of the acyl chain, which suggests an alignment of the structures forming a network stabilized by intermolecular hydrogen bonds. In mixed systems (lipid and emulsifying materials, for example), gelation is influenced by changes in the microstructure induced by heterogeneous nucleation, high crystallization kinetics, polymorphic habit modification and higher mesh density. Such changes in crystallization characteristics result in distinct networks capable of immobilizing the continuous lipid phase and originating the organogels [28].

Depending on the type of structuring element and the connections made for network formation, organogels with different properties can be formed affecting the characteristics of the product in which it is applied. The size and shape of the crystals formed by TAG can be controlled through cooling and shear and the interactions determine the mechanical properties of the network. When a large amount of structuring agent is used, a firm and dense network can be formed according to the desired profile, as well as the fluid texture organogels, whose production is made with the interaction of high and low melting TAGs [25].

The use of diacylglycerols and monoacylglycerols results in softer organogels, and, regardless of the compound, the longer the chain length, the greater the firmness of the gel obtained. Waxes, for example, have long chains and, a small amount of the material is already capable of forming a three-dimensional self-sustaining network. In addition, emulsifiers such as sorbitan monostearate, lecithin and sorbitan tristearate produce viscous solutions in edible oils, and viscosity increases with increasing concentrations of structuring agents [25].

Organogels demonstrate the potential to improve the physical characteristics of a product for industrial use without increasing the content of saturated fatty acids or trans fatty acids, making possible the development of products with reduced levels of saturated fatty acids, maintaining their sensory characteristics of texture and taste [21].

In addition, another interesting application of the organogels relates to the inhibition of the migration of oil into food products containing solid and liquid lipid phases such as in chocolates. It is expected that, through the immobilization of the liquid fraction, the mobility of the TAG is reduced, avoiding the modification of polymorphic forms, as occurs in the phenomenon of fat bloom, in bars and chocolate fillings [22].

7.1 Organogels rheology

Rheology is the branch of physics that studies the properties of flow and deformation of matter. The formulations of some materials cannot be differentiated into solids or liquids with clarity, so that the rheological property of interest in these cases is viscoelasticity, which occurs in the case of organogels, which are difficult to characterize materials, as they have solid and liquid properties at the same time. The determination of the rheological parameters can help in the characterization of the materials produced and in the understanding of the physico-chemical nature, besides allowing the understanding of the effects of the components of the formulation and the temperature used in the stability of the material [29].

Analysis of rheological behavior can be performed through parallel plate or cone-plate systems, with a small amount of sample deposited between the plates, one of which rotates and the other is fixed. Such a configuration enables to control the rotation and the calculation of the shear rate. The material then exerts a force of resistance to movement, which is measured as torque by the equipment [30].

Fluids may have newtonian, pseudoplastic, dilatant or plastic characteristics according to their behavior in relation to deformation or flow (Figure 2) [31].
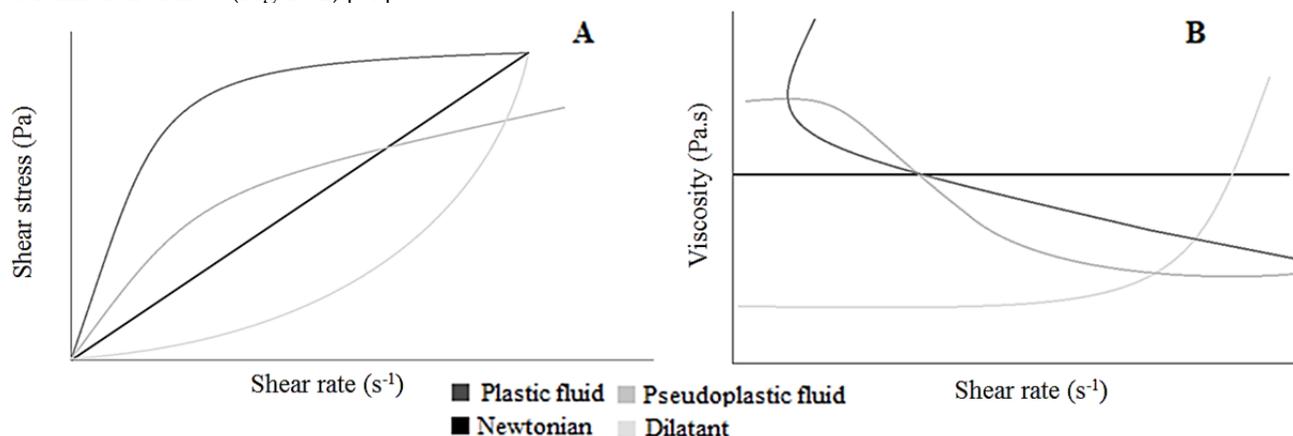
Fig. 2 Fluids classification through the behavior in relation to shear rate and shear stress (A) and shear rate and viscosity (B).

In a study performed by WRIGHT; MARANGONI [32], the profile of a vegetable-oil-based organogel, added with ricinoleic acid, was evaluated through the characterization of crystallization kinetics, microstructure, X-ray diffraction and the rheology of the gel . With the latter, it was possible to classify and identify the influence of various concentrations of ricinoleic acid on the behavior of the gel, which, between 1 and 5% (m:m) of concentration of the structuring agent, allowed to characterize the organogels as viscoelastic. In the study, the authors observed that changes in the rheological properties of the gel are more dependent on the structuring agent concentration than on the analysis temperature.

Lupi et al. [33] evaluated the influence of different types of oil phase (medium chain TAG and long chain TAG) on the process of gelling organogels with beeswax. Results showed that the increase in wax concentration led to higher values of storage and loss modulus (G', G") and complex modulus (*) of the organogels, which is associated with the net force formed between the oil and the structurant, increasing the strength and firmness of the gels.

Ramírez-Gómez et al. [34] produced high oleic safflower oil (OCAO) organogels containing candelilla wax (CC) and fully hydrogenated soybean oil (OSTH) as structurants in the proportions 1:15, 1:10, 2:15, 1:5, 3:10 , 2:5, 3:5 (m:m), or isolated, and evaluated them according to parameters of thermal behavior, polymorphism, microstructure and rheology. The rheological characteristics observed in systems consisting of 1% to 3% of isolated CC and 5% to 15% of isolated OSTH in OCAO classified these gels as viscoelastic. In addition, organogels with smaller crystals (high concentrations of CC) presented increase of G' compared with those structured with large spherulites (OSTH) while gels structured with interlaced platelets (2-3% CC) practically did not recover. This recovery effect to the initial state is desired for application in foods such as whipped cream and puff pastry.

8. Materials of interest for composition of organogels

8.1 Fully hydrogenated palm oil

Among the possible modifications in edible oils, total hydrogenation eliminates the double bonds of unsaturated fatty acids, forming hardfats or fully hydrogenated vegetable oils, materials used as crystallization additives in vegetable oils that may be capable of altering the polymorphic habit and crystallization behavior of the lipid matrix [17].

Hardfats play important role in the structuring of TAGs due to their insolubility, or limited solubility, and the ability to form a solid crystal lattice. The hardfat origin may affect its composition, but, in general, all the hardfats have similar melting characteristics, with a high melting point and a crystalline matrix that withstands high temperatures [24,35].

The hardfat of palm oil is characterized almost exclusively by palmitic (C16:0) and stearic (C18:0) acids, with approximate concentrations of 44 and 54%, respectively [3]. High-melting TAGs, present in fully hydrogenated palm oil, cause increased crystallization velocity, since the fatty acid chains present are average (C16:0 and C18:0) and have a high melting point, near at 65°C [35]. The presence of trisaturated TAGs and the predominance of fatty acids of higher chains enable to reduce the induction time of crystallization by acting as preferential crystallization nuclei. Hardfats obtained from rapeseed, soybean and palm oils are usually used in concentrations up to 5% in addition to the continuous lipid phase to increase the rate of crystallization [17].

Oliveira et al. [36] evaluated the behavior of fully hydrogenated palm, soybean, cotton and crambe oils at various concentrations added isolately in palm oil. As a result, they observed that the addition of these hardfats reduced the induction time of crystallization in all of the blends, while increasing the thermal resistance of the obtained lipid bases.

Santos [37] evaluated the performance of the palm oil hardfat at the concentrations of 1, 3 and 5% and of soy lecithin (1%) in the crystallization profile of refined palm oil and mixtures of palm oil with palm olein (25, 50 and 75%) and observed that the palm hardfat reduced the induction period with consequent acceleration of the crystallization rate and from the synergism between soybean lecithin and palm hardfat in the consistency, both acting positively as structuring agents.

The palm hardfat is allowed for use as a structuring agent in foods, however, due to its composition of saturated fatty acids (palmitic and stearic acid), it should be added in small proportions in such a way not to increase the saturated fatty acids content in the organogel and in the final product.

8.2 Candelilla wax

Vegetable waxes are defined as a mixture of long chain non-polar compounds, including primarily fatty acid esters with long chain alcohols and only one functional group [38,39]. Waxes may be natural or synthetic, and the natural waxes are found on the surface of plants, protecting them, and they are approved for use in food as ingredients or additives according to the Food and Drug Administration [40].

The candelilla wax, *Euphorbia cerifera,* of the Euphorbiaceae family, originates from shrubs in northern Mexico and southwestern United States of America. The shrub is rarely attacked by pests and diseases and much of its production is directed to the market. The wax present in candelilla provides moisture barrier, being of paramount importance to prevent the dehydration of xerophytic plants. Their composition has 49-50% of *n*-alkanes having 29-33 carbon atoms, 20-29% high molecular weight esters, 12-14% sterols and alcohols and 7-9% free fatty acids [41,42].

Because it is a vegetal product, the wax extracted from the candelilla can present variations due to the seasonality and characteristics of the planting site. A 1995 study compared candelilla waxes grown in Texas (USA), Arizona (USA), Chihuahua (Mexico) and Durango (Mexico). The waxes showed diverse composition in hydrocarbons, being the biggest difference observed in the plant harvested in Arizona. In general, waxes have from 45 to 52% hydrocarbons predominating with alkanes and alkenes; and the remaining material is composed of esters, alcohols and resins [42].

The presence of *n*-alkanes in candelilla wax is what guarantees its structuring property, since these compounds act as self-assembly agents in several apolar arrays, forming crystalline networks with chips format. These chips are joined and form the three-dimensional network that confers the macroscopic characteristics of the obtained organogels [43].

Candelila wax is mainly used in the cosmetics industry for the production of lip protectors and lotions in bars and in the paint industry for the manufacture of varnishes. In addition, it has been used to replace carnauba wax and beeswax in different food systems, due to its composition that allows the development of edible organogels through dispersions of candelilla wax in vegetable oils [39,44].

Vegetable waxes, mainly candelilla and carnauba wax, are promising structuring agents for liquid oils, as they are commercially available and result in low cost, considering the amount needed for gelation. The three-dimensional network formed by candelilla wax presents small crystals with low spatial distortion, larger surface area and small pores capable of immobilizing the oil phase. In addition to the concentration and the particularities of the waxes, external factors, such as shear and cooling rate, affect the formation of the network and the ability to bond between wax and oil. However, due to the versatility and thermal reversibility of organogels obtained with wax, its use has been exploited in different applications such as fat reduction in ice cream, margarine and other food systems [20,45,46].

In recent studies on the structuring property of candelilla wax, Toro-Vazquez et al.[44] evaluated the incorporation of about 1% of wax in safflower oil, analyzing later the thermodynamic properties of the mixture. Hwang et al. [47] observed that candelilla wax associated with rice bran wax showed good structuring properties, further revealing that small amounts of vegetable waxes can replace lipid raw materials with high trans or saturated fat contents. In recent studies, Hwang et al. [48] analyzed the formation of organogels in soybean oil using sunflower wax and concluded that the esters present in the wax were important contributing factors for the construction of the formed three-dimensional network.

Rocha et al. [39] compared the effect of adding sugarcane wax and candelilla wax to 4% soybean oil concentration. Both showed the capacity to form organogels, however, the rheological properties and the compression/extrusion analysis showed that the organogel formed by candelilla wax had higher mechanical resistance even under shear, which could be proved by microscopy under polarized light in which the organogel presented a more organized network. The authors attributed the results to the differentiated chemical composition of the waxes used, especially in relation to chain size and the presence of alcohols that can affect the interaction of the structurant with the liquid phase.

Consumption of candelilla wax is allowed within the limits of the legislations, because its ingestion is considered of low toxicity since the wax compounds are absorbed through normal metabolic pathways, without there being accumulation in the body. Hence, recent studies have indicated that candelilla wax is safe for human consumption [49].

8.3 Sorbitan monostearate

Sorbitan monostearate (SMS) is a non-ionic hydrophobic surfactant, produced by esterification of sorbitol with stearic acid. SMS is characterized as a granular solid that is dispersed in organic phases by heating to 60ºC, resulting in an opaque, whitish suspension with smooth textured gel. In cooling, the affinity between the solvent and the SMS decreases allowing the self-assembly mechanism of the system, in which the molecules of the emulsifier aggregate forming a three-dimensional network that immobilizes the solvent and is therefore able to form organogels in a variety of vegetable oils. In microscopic analysis performed by MURDAN; GREGORIADIS; FLORENCE [50] the SMS presented aggregates of tubular structures, cylindrical and elongated.

The addition of SMS in organogels as structuring agent has been made in formulations for the pharmaceutical, cosmetic and food industry. For food purposes, the use of SMS is allowed by the FDA as a food additive with a maximum content corresponding to 1% of the weight of the finished product and guarantees greater thermodynamic stability for long periods [14,21].

Sorbitan esters are generally composed of a mixture of fatty acids of different chain lengths and sorbitol molecules, as shown in Figure 3. Through this configuration, SMS is considered an emulsifier capable of influencing the delay of the polymorphic transitions in the crystallization of TAG [51]. In initial studies with oils and fats, which present a complex mixture of TAGs, the addition of 5% sorbitan esters to cocoa butter promoted the polymorphic transition from the β-form to the βV form and prevented the transition from βV to βVI, making possible a cocoa butter with presence of polymorph βV, which is of great importance to control the visual defect denominated fat bloom that occurs in chocolates [24,52].

In an in-depth study on the effect of the addition of SMS as a crystallization modifier on chocolate production, MASUCHI [53] observed that with the addition of SMS, even at minimum concentrations (about 0.5% m:m) it was possible to significantly modify the crystallization and microstructure of the cocoa butter, being effective in the modulation of the crystallization and delaying the appearance of fat bloom.

From the mechanism of co-crystallization, SMS acts as a modulator of the crystallization due to the molecular similarity with the TAGs of the cocoa butter, which are composed mainly of palmitic, oleic and stearic acids. When evaluated with continuous lipid phase, after heating to about 60°C, the cooling of the system decreases the solubility of the SMS in organic solvents as the lipid phase, forming gel structure [53,54]

Recently, SAGIRI et al. [55] described the effects of the addition of SMS to the mustard oil. Concentrations of 1 to 22% of SMS were used and with this, it was verified that the minimum required concentration of isolated SMS to immobilize the mustard oil was 17% (m:m), being able to render the system semi-solid. The density of the net formed, observed by microscopy, was proportional to the amount of structuring agent added to the oil, that is, the higher the SMS content, the denser the network. Such modification also ensured an increase in the mechanical stability of the organogels produced.

STAHL [56] analyzed the effect of incorporation of SMS associated with hardfat of soybean oil in blends of linseed oils with palm oil in different proportions. Both structuring agents, at 3% concentration, demonstrated the ability to structure lipid matrices with high levels of unsaturated fatty acids, with positive effects on solids content, crystallization kinetics, consistency, thermal behavior, microstructure and polymorphism. Such an effect can be attributed to the presence of stearic acid in the SMS which could favor its co-crystallization with TAG by incorporation on the surface of the crystals, limiting subsequent agglomerations.

OLIVEIRA et al. [57], in turn, observed the combined effect of structuring agents of the self-assembly type, in this case the SMS, with crystalline particle-type structuring agent, represented by the fully hydrogenated canola oil (*hardfat* of canola oil). In the work, mixtures containing palm oil and canola oil were made in proportions of 100:0; 75:25 and 50:50 (w:w) with subsequent addition of 6% structuring agents (50:50 OCTH:SMS), resulting in increased thermal resistance and consistency of lipid bases, which showed synergism and efficacy of OCTM and SMS. The authors verified that the association of self-assembly and crystalline particles structuring agents leads to an optimization of the lipid structuring process, allowing a reduction in the amount of each structuring element, obtaining real organogels.

The consumption of this structuring agent is allowed according to the National Library of Medicine of the United States of America (NLH), it is considered a non-carcinogenic compound that is not retained by the body and is eliminated through the urine [58].

9. Application of organogels in food

The application of organogels has been studied for some years. In the food industry, organogels have the potential to be applied in order to minimize the migration of oils into multi-component foods such as filled chocolate, margarines, baked goods (such as biscuits and cookies), puff pastry and spreads, in addition to ensuring adequate texture and consistency without the addition of saturated or trans fatty acids [21,22].

In 2013, HWANG et al. [59] have developed organogels of vegetable waxes and soybean oil for application in margarines. The waxes used were candelilla wax, rice wax and sunflower wax, in isolation. The study demonstrated the efficacy of the use of oils rich in unsaturated fatty acids, such as soybean oil, ensuring greater wholesomeness to margarine and spreads obtained with the addition of waxes.

CHAVES [60] produced reduced margarines in saturated fatty acids (from 17% to 36% reduction in final product compared with the conventional) with addition of soybean oil organogels or high oleic sunflower oil containing candelilla wax, interesterified fat and monoacylglycerols. The produced margarines presented greater stability in comparison with the commercial margarines and the use of candelilla wax was essential to obtain this result, since the test with absence of candelilla wax showed oil exudation. In general, the parameters of consistency, spreadability, emulsion stability in relation to temperature fluctuations and hardness were similar to commercial margarines.

In similar study, YILMAZ; OGUTCU [61] produced organogels from hazelnut oil and olive oil using bee and sunflower waxes as structuring agents, also for margarine application. In this case, the authors achieved characteristics very similar to commercial margarine. The sensory evaluation of the final product indicated that about 50% of the testers would possibly buy the product.

Also using waxes as a structuring agent, ZULIM BOTEGA et el [62] have developed organogels to replace the lipid fraction in ice cream. Blends containing 10% wax (from candelilla, rice or carnauba) were evaluated with 90% high oleic sunflower oil and glycerol monooleate as emulsifier. In this case, the use of organogels as lipid fraction was able to confer adequate structure to the ice cream, characterizing it as similar to conventional.

The substitution of shortenings by organogels in bakery products has also been performed to reduce the saturated and trans fat content. In studies performed by JANG et al. [63], the lipid fraction of cookies was replaced by organogel from canola oil and candelilla wax, whose hardness was lower than that of conventional shortening at room temperature, as well as the results observed in rheological parameters. When added to the cookies, the organogel product generated less bursting strength, resulting in greater softness, a feature different from that desired for commercial cookies. However, the fatty acid composition indicated that with the substitution of shortening, there was a 92% increase in the content of unsaturated fatty acids.

In a similar study, organogels containing 5% candelilla wax in sunflower oil were also added in cookies resulting in very similar parameters, with softer, less crunchy cookies and with changes in the rheological parameters,

characterizing them as more fluid, and expressive increase of the content of unsaturated fatty acids [64]. In both studies, the cookies sensory analysis test was not performed.

BEMER et al. [65], produced organogels with soybean oil and 10% structurants (rice wax or ethylcellulose) for application in cream cheese. In relation to the conventional product, to that added organogel resulted in a reduction of 90% in the content of saturated fatty acids. The rice wax provided a texture very similar to the commercial cream cheese and, in contrast, the organogel with ethylcellulose showed lower adhesiveness and modulus of elasticity than the commercial parameters. Thus, the study evidences the applicability of organogels containing vegetable wax to the development of healthier products.

Therefore, it is observed that studies on the application of organogels are still scarce, but extremely current and relevant in the area of lipid technology. The development and characterization of organogels are therefore an important technological alternative for obtaining lipid bases with a technological profile suitable for the application in several food, free from trans isomers and with a reduction in saturated fatty acid content.

10. Conclusion

Due to the deleterious effects attributed to the high consumption of saturated and trans fatty acids, organogels present themselves as a potential technological alternative suitable for application in food products, minimizing the migration of oils into multi-component foods, guaranteeing the desired technological characteristics in products such as filled chocolate, margarines, ice cream, spreads, cream cheese and baked goods such as cookies, and puff pastry. These applications, already described in the literature, were able to reduce the content of saturated fatty acids, without the presence of trans fatty acids, demonstrating the wide diversity for the application of organogels in food products according to the characteristics of the obtained systems.

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