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Chapter

Conventional and Unconventional Crystallization Mechanisms

Kamila Ferreira Chaves, Thaís Jordânia Silva, Maria Aliciane Fontenele Domingues, Daniel Barrera-Arellano and Ana Paula Badan Ribeiro

Abstract

Understanding the crystallization behavior of fats and oils is essential to ensure certain desirable characteristics in a given industrial application. In recent years, some advances in the structuring of lipid phases have enabled a direct influence on the food properties. The structuring mechanisms of lipid bases can be classified as either conventional or unconventional. Conventional crystallization mechanisms consist of nucleation, growth, and maturation of the crystals, thus resulting in a crystalline lattice. Co-crystallization or seeding agents and emerging technologies such as ultrasound can be used to aid in crystallization and improve the physical properties of fats and oils. Unconventional mechanisms bring organogel technology as a trend, which consists in the use of self-assembly agents to entrap the liquid oil, resulting in a structured gel network. In this chapter, the formation process of crystalline networks and gel networks will be presented in stages, highlighting the main differences related to the mechanisms of formation and stabilization of both types of networks.

Keywords: conventional crystallization, unconventional crystallization, crystallization mechanisms, crystalline networks, gel networks, seeding agents, emerging technologies

1. Introduction

Edible oils and fats are essential nutrients in the diet as they provide essential fatty acids and energy. In addition, they have important functions in the production of processed foods. These ingredients are directly related to texture, stability, aeration, and nutritional features of the products [1, 2]. Some fats used in food are known by the term shortening, also known as plastic fats. Selection of the best shortening is based on formulations (product to which it is intended), functions, and process conditions. The production of shortening is related to the types of fats and oils used and the way in which they crystallize and form solid networks. This is because solid crystalline fat networks are responsible for providing the expected physical macroscopic functions of the various types of shortening systems, due to the way they melt and to the hardness, consistency, and complacency of the network [3].

Oils and fats are one of the three food macronutrients, represented by triacylglycerol (TAG) molecules, formed by an ester bond between glycerol and three fatty acids. TAG crystals are known to show polymorphism, which is the ability of

a substance to have more than one structure or crystalline form. As the physical properties of fat crystals, such as melting point and rheology, are important for food texture, polymorphic control of fat crystals is crucial in the food industry, and it is thus necessary to understand the crystallization mechanisms of TAGs.

Crystallization consists of an arrangement of the system as a result of a driven force, characterized by the total or partial restriction of movement caused by physical or chemical bonds between TAG molecules. Due to the complexity of this system, TAGs can be compacted in different ways. This crystallization has implications in the industrial processing of foods, since these depend on fat crystals in products like margarines, chocolate, spreads, baked goods, etc. [4, 5].

2. Lipids

Lipids are defined as compounds soluble in organic solvents and insoluble in water. These compounds are represented by oils and fats. Chemically, vegetable oils and fats are mainly composed of TAGs and may contain small amounts of diacylglycerols, monoacylglycerols, free fatty acids, phospholipids, waxes, and unsaponifiable constituents [6].

Glycerol has three positions in its molecule (*sn*-1, *sn*-2, and *sn*-3) in which the fatty acids are esterified to form the TAG. The features of these fatty acids influence the physical properties of oils and fats: (i) in relation to unsaturation and saturation: saturated fatty acids have a higher melting point compared to unsaturated ones, since unsaturation impairs the packing of molecules; (ii) in relation to the geometric isomerism: it refers to the possible arrangements of the hydrogen atoms around the double bond, presenting the *cis* or *trans* form. *Cis* bonds reduce the melting point due to folding of the molecule, impairing packing. Conversely, fatty acids in a *trans* configuration have a melting point close to that of saturated fatty acids, due to torsion in the molecule, making it linear; and (iii) in relation to chain size: the longer the chain, the higher the melting point. Physically, oils are liquid at room temperature, while fats are solid, semi-solid, and plastic at room temperature. Therefore, the composition in TAGs determines the physical and functional properties of oils and fats, affecting the structure, stability, taste, and the sensorial and visual characteristics of foods [5].

3. Crystallization mechanisms

3.1 Conventional crystallization

Crystallization, melting, and recrystallization of lipids are first order transitions of interest in food systems that affect the shelf life of food and food ingredients. The crystallization properties of food components may be highly complex due to soluble-solvent interactions, mixture of miscible components, and polymorphic transitions. The production of solid fats, spreads, and chocolates is an excellent example of the use of first-order transition behaviors of food systems to manipulate properties in processing, structure formation, and application performance [7]. Understanding the development of structures and the control of the crystallization of food components has evolved over the years, but there is still much to learn.

In lipids, the conventional crystallization process is fundamentally important to understand what happens while processing foods such as chocolates, spreads, bakery products, margarines, ice cream, etc. How can these crystals have such a great influence on the quality of a product? We can propose ice cream as an example.

When consuming an ice cream, we want it to be creamy without crystals leaving a sandy sensation in the mouth. Another classic example is chocolate, as a properly crystallized cocoa butter of good quality, which provides a shiny and smooth chocolate that melts homogeneously [8].

Macroscopic properties of lipids in foods are particularly influenced by the microstructure of fats. Therefore, it is important to consider the effects of the microstructure for subsequent analysis of macroscopic properties. The formation and growth rate of the crystals and the polymorphic transformations are important to determine the function and application of oils and fats [4]. Therefore, understanding crystallization is fundamental to obtain products with adequate functions, texture and sensory qualities and that are physically stable.

The following sections will address the mechanisms that occur in vegetable fats during their crystallization. We will also understand that some techniques can induce or delay this crystallization in different ways, in order to achieve the industrially desired result.

3.1.1 Definitions and mechanisms

Before discussing the conventional crystallization mechanism of vegetable fats, we need to define some concepts that are fundamental for a good understanding of the subject. We define conventional crystallization as an arrangement of the system characterized by total or partial restriction of movement, caused by the physical or chemical bonds between the molecules of TAGs. These bonds will lead to what we call crystals, which are molecules arranged in fixed patterns. Its high degree of molecular complexity allows the same set of TAGs to be compacted into several different and relatively stable structures [9, 10].

We can say that the crystallization behavior involves four phases: nucleation (formation of a crystalline phase in the liquid phase through the organization of TAGs in a crystalline network, that is, molecules in the liquid state bind to create a stable nucleus), growth (caused by the inclusion of other TAGs in the existing crystalline network), recrystallization (structural and chemical change of the crystals during storage), and polymorphism (which controls the order of packing of TAG molecules in the crystals). Before forming the first crystals, the system, in its liquid state, needs to reach the supersaturated zone, in which there is a driving force for crystallization [11, 12]. From this point, crystallization starts.

3.1.1.1 Nucleation

It starts with the appearance of a driving force to overcome the energy barrier for crystallization. As a result, molecules in the liquid state somehow bind to create a stable nucleus. Nucleation can be classified as (a) primary nucleation (homogeneous or heterogeneous) (**Figure 1**) and (b) secondary nucleation. Homogeneous primary nucleation occurs with the binding of isolated molecular species, which form dimers and trimers, and subsequently continues the accumulation process until a potential nucleus can be formed. That is, it is a molecular arrangement in a crystalline network, without external aid.

Heterogeneous primary nucleation occurs when the local arrangement of molecules to form the nucleus arises from interactions between the solid particle and the supersaturated fluid, by supplying external energy. Secondary nucleation is the formation of a new nucleus in the presence of existing crystals, which may occur if crystalline microscopic elements are separated from an already formed crystalline surface, resulting in fracture of crystals in small stable nuclei [5, 8]. Once a crystal core is formed, it starts growing due to the incorporation of other molecules of

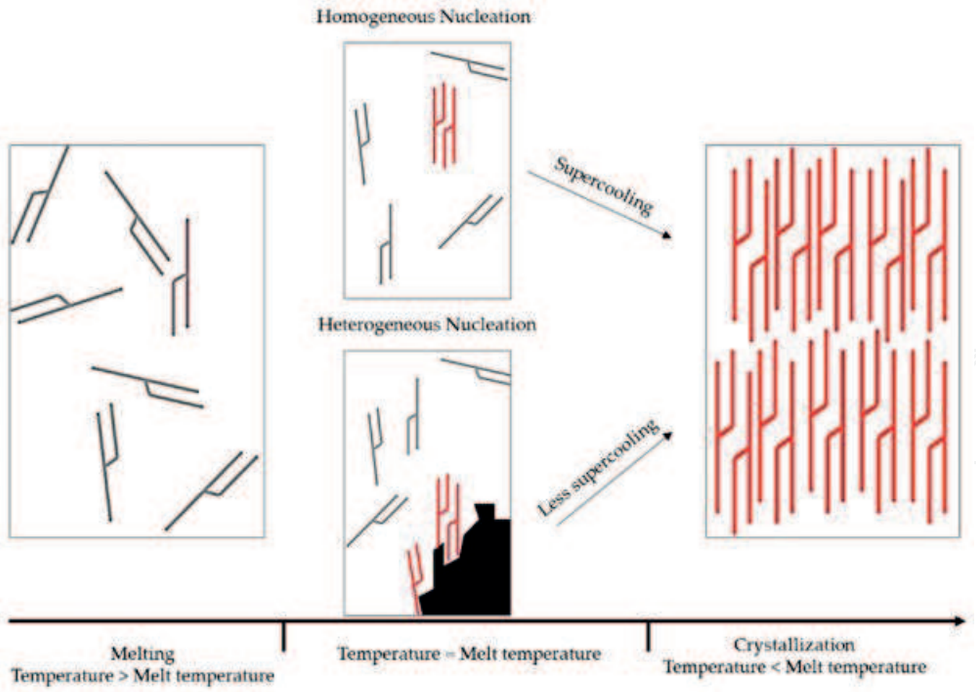

Figure 1.
Nucleation mechanisms: crystal embryo formation in homogeneous nucleation and seeding or co-crystallization in heterogeneous nucleation (adapted from [13]).

the adjacent liquid layer, which is continuously filled by the supersaturated liquid surrounding the crystal [12].

3.1.1.2 Growth

According to the theory, crystalline growth occurs through two features: (1) surface of the growth process and (2) transport process in the face of the growing crystal [14]. The mechanism is based on how the face of the crystal incorporates growth units of the adjacent solution. According to Hartman and Perdok [15], for a three-dimensional crystalline face, the capture of growth units can be classified according to how many binding interactions form between the adsorbed growth unit and the surface of the crystal. If three orientations of surface bonds are involved, the incorporation is then of the kinked face type; if two orientations of surface bonds are involved, the incorporation is of the stepped face type; and if only one surface bond is involved, the incorporation is of the flat face type (**Figure 2**).

Once a crystal nucleus is formed, it starts growing due to the incorporation of other molecules of the adjacent liquid layer that is continuously filled by the supersaturated liquid that surrounds the crystal [12]. When the formed nuclei reach favorable dimensions, these elements become crystallites, and their growth depends on external (supersaturation, solvents, temperature, and impurities) and internal (structure, bonds, and defects) factors. Therefore, the crystal growth rate can vary by several orders of magnitude. Growth occurs through the binding of molecules to a crystalline surface. While the molecules are attached to the surface of a crystal, some molecules are also deactivated. There is a continuous movement of molecules at 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 to the viscosity system [5, 12]. Unless there is a kinetic constraint, growth continues until the system reaches equilibrium (driving force for crystallization of zero and maximum volume of the phase of the crystals) [8].

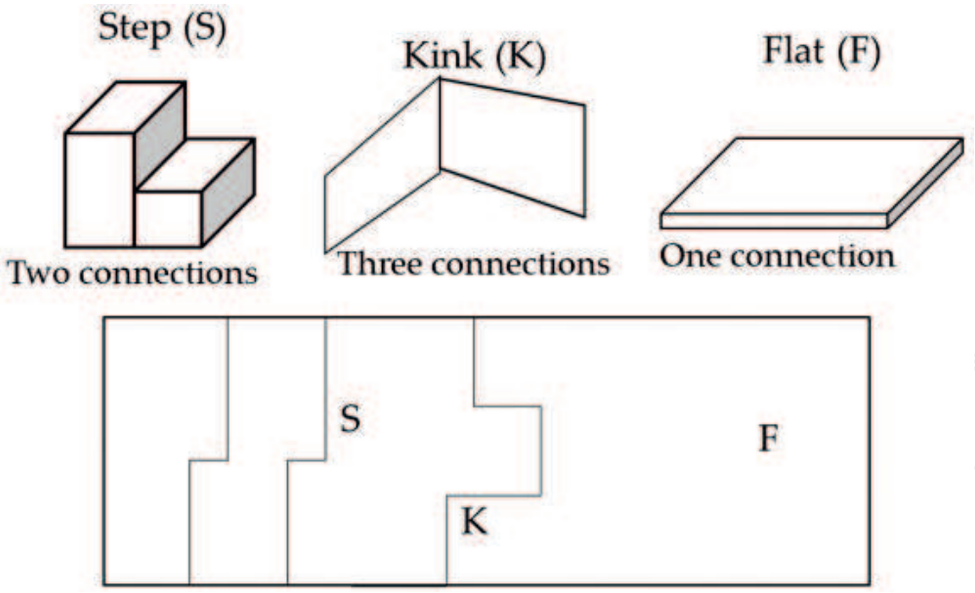

Figure 2.
Classification of surface contacts according to growth theory (adapted from [15]).

3.1.1.3 Recrystallization

The final stage of crystallization in food occurs during storage, when crystals undergo a recrystallization step [8]. This phenomenon can be defined as a change in the size, shape, orientation, and perfection of the crystals [16]. Basically, in this stage, small crystals, which are more soluble, disappear and larger crystals grow. The concern with this step is related to the changes in the products during their storage, such as fat bloom in chocolates and coatings and oil exudation in fat-rich products [12].

3.1.1.4 Polymorphism

When discussing lipid crystallization, we must relate this phenomenon to one of the most important physical properties, which is polymorphism. Polymorphism can be defined in terms of the ability to present different unit cell structures due to several molecular packages [5]. In lipids, there are three specific types of subcells (the smaller periodic structure that exists in the current cellular unit, which is defined as the transverse mode of packing of the aliphatic chains in the TAGs), the polymorphs: α, β′, and β [4]. The α form is metastable, with hexagonal chain packing. The β′ form has intermediate stability and orthorhombic perpendicular packing. Crystals in the β′ form show greater function, since they are smoother and provide good aeration and creaminess properties. The β form has greater stability and triclinic parallel packing. The melting temperature increases with increasing stability (α → β′ → β) due to differences in molecular packing density [5, 17]. The crystal structures also differ in chain length, which illustrates the repetitive sequence of acyl chains in a unit cell along the axis of a long chain. The chain length structure ranges from double (DCL) to triple (TCL), fourth (QCL), or hexa (HCL). In addition, the conformation of the glycerol group also influences the phase behavior of fats. Two typical glycerol conformations, fork type and chair type, have been observed in TAG crystals. The fork-like conformation is favored by the presence of two identical fatty acids at positions 1 and 3 of the glycerol, forming a symmetrical TAG. On the other hand, the chair-type conformation is favored in asymmetric TAGs. Neighboring molecules of TAG crystals are stacked in layers, with the parallel

hydrocarbon chains packed together and arranged more or less perpendicular to the parallel planes of the glycerol groups and to the methyl terminal group planes. The distances between these molecules characterize the short spacings and the long spacings, providing the polymorphic properties and melting point of each type of fat. The choice between the fork- or chair-like conformation is dictated by the need to accommodate fatty acids of different chain lengths and the distortions introduced by the double bonds [18, 19] (**Figure 3**).

3.1.2 Crystallization modifiers

The crystallization process can be modified using techniques that change the kinetics of the crystals, such as the use of additives and ultrasound.

3.1.2.1 Additives

Lipophilic additives are used as they influence the volume properties (consistency and texture), promoting or inhibiting crystallization. These compounds provide a modeling effect, i.e., seeding nuclei. For example, a higher melting point additive with chemical and structural similarities to the lipid is used as a seeding nucleus for heterogeneous crystallization [20]. Examples of additives that may promote or inhibit crystallization are minor lipids, such as diacylglycerols, monoacylglycerols, free fatty acids, phospholipids, and sterols. These lipids can interact with TAGs in the growth stage, causing a structural competitive effect or permanent incorporation into the crystalline structure, affecting the crystallization rate, polymorphic forms, and microstructure of the crystals, positively or negatively [21].

Another technique that is being increasingly used is seeding. It consists of the addition of a solid material with crystallization nucleating agent properties. The incorporation of crystallization seeds into liquid fats can promote two effects associated with the control of crystallization by the availability of numerous additional nuclei and/or surfaces for crystal growth. In addition, it may promote specific polymorphic forms [21].

The addition of emulsifiers changes the supersaturation characteristics of the solution and consequently its solubility, and thus, the incorporation of growth units on the surface will also change. At low supersaturations, growth occurs by the incorporation of the flat face type, and, in general, the free energy (ΔG) decreases

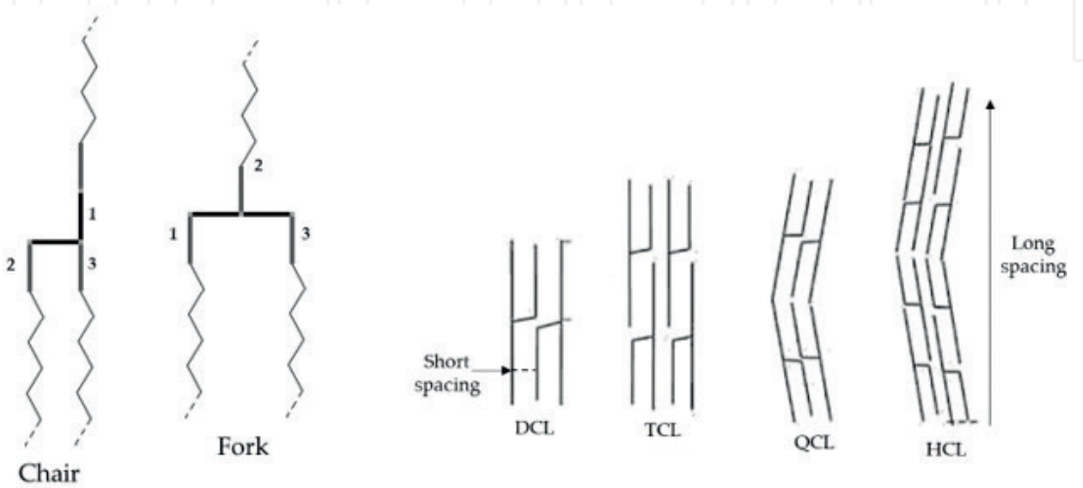

Figure 3.
Conformation of glycerol groups in triacylglycerol crystals and chain length structures of triacylglycerol crystals (adapted from [18]).

according to the sequence kinked < stepped < flat [21]. Thus, the mechanisms of co-crystallization and seeding occur, leading to the template effect of the emulsifiers (**Figure 4**).

3.1.2.2 Ultrasound

This technique has been noted as an excellent alternative to promote crystallization, since the ultrasonic energy is sufficient to promote nucleation and growth by increasing the transfer of heat and mass. Through manipulation of nucleation and growth, ultrasounds can potentially provide improved control for the assembly of crystal structures in foods to control texture or improve separation [8]. It is believed that these ultrasonic effects are superior to conventional agitation to control and stimulate the reaction rate, supersaturation level, nucleation, and crystal growth [22].

Care should be taken in relation to the intensity of ultrasound used, since the crystalline structure is highly dependent on the intensity of the ultrasound. For example, a palm oil where the ultrasound was applied at an intensity of 30 dB had little effect on kinetics but prevented the formation of large spherulitic crystals. When this intensity was increased to 35 dB, it produced smaller, more uniform crystals that tend to clump and fall to the bottom of the cell. A further increase in intensity to 40 dB, below the cavitational threshold, produced a uniform product of very small crystals, suggesting that there are numerous nucleation sites that produced crystals simultaneously [23].

The effects caused by the ultrasound include: (i) faster primary nucleation, which is quite uniform through the sonicated volume; (ii) relatively easy nucleation in materials that are otherwise generally difficult to nucleate; (iii) start of the secondary nucleation; and (iv) production of smaller, purer crystals of more uniform size. In addition, ultrasound can reduce clumping of crystals. The shock

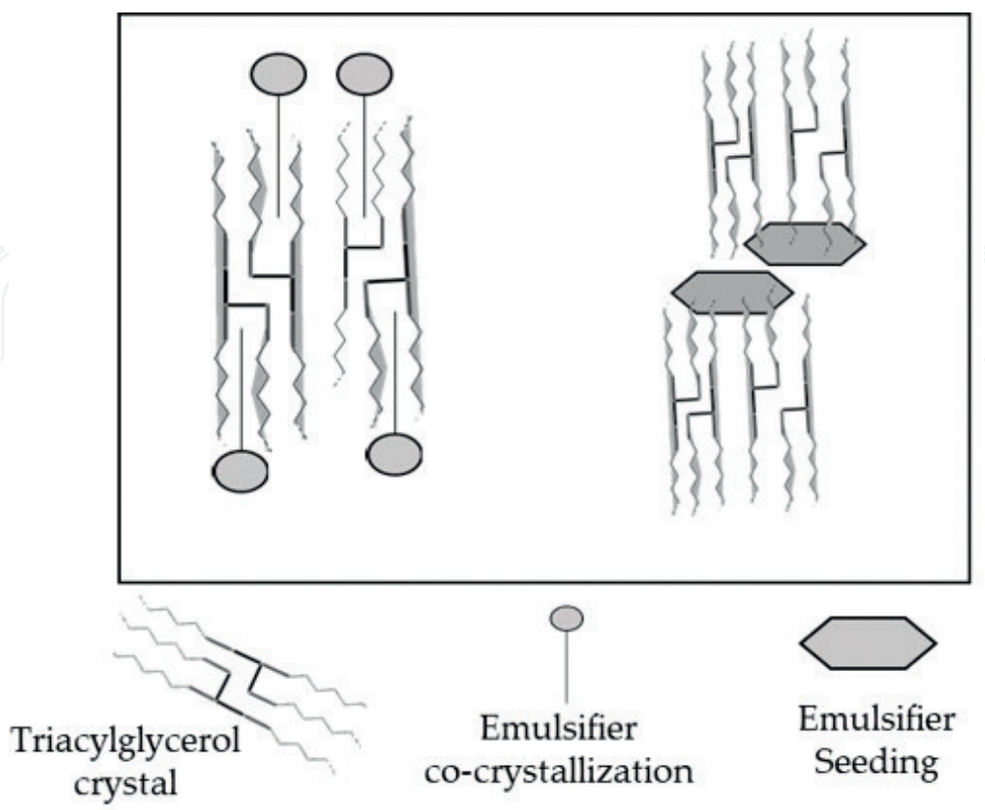

Figure 4.
Template effect of emulsifiers: co-crystallization and seeding.

wave, which is caused by cavitation, decreases the contact between the crystals, preventing clumping, by controlling the population of local nuclei. The induction time is defined as the time elapsed between onset of supersaturation and appearance of crystals and decreases as supersaturation increases. This induction time is drastically reduced by the presence of sonication. This effect is more significant at low absolute supersaturations [24].

3.2 Unconventional crystallization

Studies with organogels led to the development of many applications in the food area, such as chocolate filling, margarines, baked products, such as biscuits and cookies, pastries, spreads, sausages, ice cream, yogurt, unprocessed and processed cheese, mayonnaise, and sauces, among other products [25–28]. Considering this, it is crucial to understand how unconventional crystallization occurs.

Many organogels are more desirable to consumers since they have a better nutritional profile than conventional fats. Therefore, organogel technology seems to be a potential solution for the reduction of saturated fatty acids and possibly the elimination of trans-fatty acids from processed foods [26, 29, 30].

This technology is feasible in comparison to the technologies currently used, since it does not cause any chemical changes in the structure of fatty acids and TAGs and maintains the nutritional features of the oil; in particular, it maintains unsaturated fatty acid contents and natural regiospecific distribution without increasing the AGS content [31].

3.2.1 Definitions and mechanisms

Organogels are a class of materials that can hold large volumes of organic liquids in self-assembled networks and have many practical applications in the pharmaceutical, chemical, and food industries regarding lipid technology [32]. Organogels are formed by structurants of low molecular weight and some organic solvents that are supported, through a three-dimensional network, forming the gel. Since organogels are biodegradable, they can be used in drugs as protein carriers and vaccines for example [33–35].

The formation of these structures through supramolecular assembly is of great interest, since they can form semisolid phases that are produced at low cost [32]. Several researchers have focused their studies on the properties of structurants to form organogels [22, 36–38].

In unconventional structuring, lipid systems composed of unsaturated TAGs, such as liquid or semi-solid vegetable oils, can be structured as gels, forming continuous networks of small molecules that assemble in liquid crystals, micelles, or fibrillar networks formed from aggregates of micelles, developing inverse bilayer structures in the form of rods [39].

Organogels can be structured forming a fibrous 3D network, where the solvent is trapped in the structuring matrix, avoiding the flow of solvent. The network is stabilized by weak interactions between the chains, such as hydrogen bonds, van der Waals forces, and π staking [40–43]. Although it is known that organogels are formed through weak intermolecular interactions between the structurant molecules, which generate three-dimensional networks [44], there is still a lack of fundamental understanding of the type of interactions that are required [32].

The physically driven process of structuring organogels depends on many factors, such as structural adjustment of structurant molecules, solvent effects, concentration, temperature, use of ultrasounds, and shear. When these factors change, the structuring properties are affected due to the precise balance between

the interaction of the structurant molecules, the interaction between the solvent and the structurant, and the applied external stimulus [45, 46].

The structurants are insoluble in almost all solvents at room temperature, and the solvent-structurant and structurant-structurant interactions are the main force for the formation of organogels. However, they dissolve after heating and jellify after cooling; thus, the gelation process is an equilibrium between dissolution and precipitation in the solvents [47].

Organogel networks may range from the assembly of surfactants into solution by physical interactions (e.g., micellization, lyotropism, and crystallization) [48], also known as molecular organogels, to the formation of flexible polymer networks (e.g., swelling), known as polymer organogels [49]. The molecular organogels known today are at the interface between complex fluids [50] and solids and, regardless of the nature of the structure, are composed of thermoreversible semi-solid materials [32].

3.2.2 Structuring modifiers

The group of molecular organogels can be subdivided according to the mode of self-organization of the structurant in liquid crystals [51], platelet crystals, elliptic networks [52, 53], and inverted micelles [54, 55].

Several solvent parameters have now been used to correlate with gelation ability [56], such as protic, dipolar aprotic, and apolar aprotic (low polarity), which were too broad to quantify solvent effects [57]. More specifically, solvent parameters are divided into three categories: physical properties, solvatochromic properties, and thermodynamic properties, including dielectric constant, Reichardt ET-30 parameter [58], Kamlet-Taft parameters [59], Hildebrand solubility parameter [60], and Hansen solubility parameters [61, 62].

The structures of the organogel molecules significantly influence the resulting gelation properties. The length of the alkali chain, the position of the chiral units, the substitution groups, and the peptide sequences, in addition to the arrangement or the number of the hydrogen bonds, may influence the properties of organogels [45].

The structures can be formed from amphiphilic compounds that can self-assemble in different microstructures, such as micellar and bilayer phases, which may accumulate in different lyotropic mesophases of larger scales (hexagonal, cubic, or lamellar liquid crystalline phases) at high concentrations [63, 64]. The formation of longer structures provides viscoelastic behavior or a gel-like solution. These viscoelastic materials, created through the assembly of structurants, are described in the literature as supramolecular organogels [65]. The formation mechanism of these structures is based on the arrangement of monomeric units that bind through non-covalent bonds, such as van der Waals interactions, hydrogen bonds, electrostatic interactions, and π-π or τ-stacking [65, 66].

Two different types of packing models were discovered in non-polar and polar solvents. In non-polar solvents, an interdigitated stacking model was preferred in the self-organized 3D micromorphology of the gels, due to inverse strong hydrogen bonds and weak π-π stacking interactions. Conversely, in polar solvents, the structurant is automatically assembled in a 3D nanostructure through a stacking model due to strong π-π stacking interactions and weak hydrogen bonds [67].

In general, there are a limited number of biocompatible components known to structure lipids through the assembly of molecules [46, 68, 69].

The extensive applications of organogels are of great importance to design and study new structurants and to characterize and determine the practical applications for organogels. It is known that some organogels with excellent mechanical and optical properties are more useful for practical applications [45].

Current knowledge on assembly behavior and subsequent gel formation and the effect of salts was applied to induce the formation of networks in hydrophobic environments using an unsaturated fatty acid, oleic acid, and sodium acetate, in sunflower oil. Oleic acid alone did not provide gelation in the oil, but the addition of sodium oleate induced gel formation. In mixtures containing oleic acid, reverse micellar structures are present. The participation of the sodium oleate in the original spherical micelles of oleic acid changes the geometry and assembly behavior of the structurant. At higher concentrations of sodium oleate, lamellar crystal structures are formed. The assembly is theoretically driven largely by hydrophilic interactions between the hydrophilic head groups, as the strength of the interactions increased by the addition of small amounts of water. For water concentrations of more than 2%, the assembly was inhibited [32].

Vegetable waxes provide an ideal feature for organogels, which is more similar to the features provided by saturated and trans fats but show stability problems over prolonged periods. There is currently a clear lack of knowledge regarding the identification of ideal proportions of ceramides, fatty acids, cholesterols, and phytosterols, in terms of oil structuring, crystal morphology, and consequent suitability for applications in foods. Although carbohydrate-based gelatins were extensively studied, there are very few studies in the field of organogels [26].

4. Emerging crystallization technologies

The success of organogels in recent years in food applications continues to stimulate the interest of researchers in this area and provides a broader view [26].

A gel system is prepared by holding the solvent in the gelator matrix, stimulated by pH, heat, light, magnetic field, or ultrasound [47]. Supramolecular gels that have their structuring initiated by physical (including sonication) and mechanical (mechanical force) stimuli exhibit non-covalent interactions between the structurant molecules and show dynamic and reversible properties controlled by the stimuli, while structurants cause instant and *in situ* gelatinization in organic solvents or water with different modes and structuring results, but can lead to dynamic changes in the microscopic morphology, optical properties, etc. [45].

During the solvent-organogel transition process, changes in the conformation of the structure of the molecule can occur in thixotropic or ultrasonic organogels, but it is difficult to study these changes with the existing techniques and without crystallization data [45].

A novel low molecular weight, photoresistant organogel, based on an azobenzene derivative and which can achieve the reversible gel-solvent transition by the heat/cold process or visible/UV light irradiation, was designed and successfully synthesized. The structurant has a good gelation ability in organic solvents ranging from non-polar to polar solvents due to hydrogen bonds and π-π stacking [45].

The reversible control of the properties of the organogel through the application of heat and mechanical stimuli is often followed by transformations in the phase, morphological structure, and rheological and spectroscopic properties, which makes these organogels suitable to be used in the field of drug release and adaptive materials, among other applications [45].

5. Conclusion

This study carried out a comprehensive review on the possibilities of modification of the crystallization of lipid phases, to subsidize the knowledge of the

crystallographic, microstructural, and kinetic phenomena involved in the processes of structuring oils and fats. Different emulsifiers used in low concentrations, besides the application of ultrasound technology, are proven effective in the processes of lipid modification and represent a highly feasible option, in economic and process terms, to modulate the crystallization properties of industrial oils and fats.

In addition, the use of organogels in food applications as substitutes for trans and saturated fatty acids is highly feasible since structured vegetable oils are generally used to replace fats. Compared with conventional technological processes for the production of technical fats for food applications, the production of organogels is technologically simple, economically accessible, and inexpensive. Several oils with majority composition in unsaturated fatty acids can be immobilized. Structuring agents are used in small proportions, being commercially available and safe for consumption.

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Conflict of interest

The authors state that there is no conflict of interest.

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References

[1] Hashempour-Baltork F, Torbati M, Azadmard-Damirchi S, et al. Vegetable oil blending: A review of physicochemical, nutritional and health effects. Trends in Food Science and Technology. 2016;**57**:52-58. DOI: 10.1016/j.tifs.2016.09.007

[2] Rohm H, Schäper C, Zahn S. Interesterified fats in chocolate and bakery products: A concise review. In: Shahidi F, editor. LWT—Food Science and Technology. 2018;**87**:379-384. DOI: 10.1016/j.lwt.2017.08.076

[3] Ghotra BS, Dyal SD, Narine SS. Lipid shortenings: A review. Food Research International. 2002;**35**:1015-1048. DOI: 10.1016/S0963-9969(02)00163-1

[4] Sato K. Crystallization behaviour of fats and lipids—A review. Chemical Engineering Science. 2001;**56**:2255-2265. DOI: 10.1016/S0009-2509(00)00458-9

[5] Ribeiro APB, Masuchi MH, Miyasaki EK, et al. Crystallization modifiers in lipid systems. Journal of Food Science and Technology. 2015;**52**:3925-3946. DOI: 10.1007/s13197-014-1587-0

[6] Block JM, Barrera-Arellanos D. Temas Selectos en Aceites y Grasas. Química. Vol. 2. São Paulo, Brazil: Marcel Dekker, Inc, Blucher; 2013

[7] Roos YH. Phase and state transitions and related phenomena in foods. Food Materials Science and Engineering. 2012;**1**:1-15. DOI: 10.1002/9781118373903.ch5

[8] Hartel RW. Advances in food crystallization. Annual Review of Food Science and Technology. 2013;**4**:277-292

[9] Foubert I, Dewettinck K, Van de Walle D, et al. Physical properties: Structural and physical characteristics. In: The Lipid Handbook. Gunstone FD, Harwood JL, Dijkstra AJ, editors. 3rd ed. Boca Raton: CRC Press; 2007. pp. 47-81

[10] O'Brien RD. Oils and fats: Formulating and Processing for Applications. 3rd ed. New York: Taylor & Francis Group; 2008

[11] Patel AR, Dewettinck K. Current update on the influence of minor lipid components, shear and presence of interfaces on fat crystallization. Current Opinion in Food Science. 2015;**3**:65-70. DOI: 10.1016/j.cofs.2015.05.010

[12] Domingues MAF, Ribeiro APB, Kieckbusch TG, et al. Advances in lipids crystallization technology. Advanced Topics in Crystallization. 2015;**1**:105-132. DOI: 10.5772/59767

[13] Clercq N. Crystallization of fats and oils. In: KOI Cocoa Processing and Chocolate Production. Belgium: Ghent University; 2013

[14] Seddon KR, Zaworotko M. Crystal Engineering the Design and Application of Functional Solids. Holanda: Springer; 1999

[15] Hartman BP, Perdok WG. On the relations between structure and morphology of crystals. I. Acta Crystallographica. 1955;**8**:49-59. DOI: 10.1107/S0365110X55000121

[16] Fennema OR, William DP, Elmer HM. Low Temperature Preservation of Foods and Living Matter. Taylor & Francis; 1973

[17] Martini S, Awad T, Marangoni AG. Structure and properties of fat crystal networks. In: Gunstone F, editor. Modifying Lipids for Use in Food. Cambridge: Woodhead Publishing; 2006. pp. 142-169

[18] Garti N, Widlak NR. Cocoa Butter and Related Compounds. 1st ed. Urbana, Illinois: Elsevier; 2015

[19] Coultate TP. Food: The Chemistry of its Components. 6th ed. Cambridge: Royal Society of Chemistry; 2016

[20] Bayés-García L, Patel AR, Dewettinck K, et al. Lipid crystallization kinetics-roles of external factors influencing functionality of end products. Current Opinion in Food Science. 2015;**4**:32-38. DOI: 10.1016/j.cofs.2015.04.005

[21] Metin S, Hartel RW. Crystallization of fats and oils. In: Shahid F editor. Bailey's Industrial Oil and Fat Products. New York: Wiley Interscience; 2005. pp. 45-76

[22] Li Z, Cao J, Li H, et al. Self-assembled drug delivery system based on low-molecular-weight bis-amide organogelator: Synthesis, properties and in vivo evaluation. Drug Delivery. 2016;**23**:3168-3178. DOI: 10717544.2016.1157841

[23] Patrick M, Blindt R, Janssen J. The effect of ultrasonic intensity on the crystal structure of palm oil. Ultrasonics Sonochemistry. 2004;**11**:251-255. DOI: 10.1016/j.ultsonch.2004.01.017

[24] Castro MDL, Priego-Capote F. Ultrasound-assisted crystallization (sonocrystallization). Ultrasonics Sonochemistry. 2007;**14**:717-724. DOI: 10.1016/j.ultsonch.2006.12.004

[25] Chaves KF, Barrera-Arellano D, Ribeiro APB. Potential application of lipid organogels for food industry. Food Research International. 2018;**105**:863-872. DOI: 10.1016/j.foodres.2017.12.020

[26] Singh A, Auzanneau F, Rogers MA. Advances in edible oleogel technologies—A decade in review. Food Research International. 2017;**97**:307-317. DOI: 10.1016/j.foodres.2017.04.022

[27] Hughes NE, Marangoni AG, Wright AJ, et al. Potential food applications of edible oil organogels. Trends in Food Science & Technology. 2009;**20**:470-480. DOI: 10.1016/j.tifs.2009.06.002

[28] Moschakis T, Panagiotopoulou E, Katsanidis E. Sunflower oil organogels and organogel-in-water emulsions (part I): Microstructure and mechanical properties. LWT—Food Science and Technology. 2016;**73**:153-161. DOI: 10.1016/j.lwt.2016.03.004

[29] Garcia RKA, Gandra KM, Barrera-Arellano D. Development of a zero trans margarine from soybean-based interesterified fats formulated using artificial neural networks. Grasas y Aceites. 2013;**64**:521-530. DOI: 10.3989/gya.049113

[30] Marangoni AG, Garti N. Edible Oleogels: Structure and Health Implications. Amsterdam, Netherlands: Elsevier Inc; 2011. DOI: 10.1016/C2015-0-02413-3

[31] Sundram K, Karupaiah T, Hayes KC. Stearic acid-rich interesterified fat and trans-rich fat raise the LDL/HDL ratio and plasma glucose relative to palm olein in humans. Nutrition and Metabolism. 2007;**4**:3. DOI: 10.1186/1743-7075-4-3

[32] Nikiforidis CV, Gilbert EP, Scholten E. Organogel formation via supramolecular assembly of oleic acid and sodium oleate. RSC Advances. 2015;**5**:47466-47475. DOI: 10.1039/c5ra05336f

[33] Uzan S, Barış D, Çolak M, et al. Organogels as novel carriers for dermal and topical drug delivery vehicles. Tetrahedron. 2016;**72**:7517-7525. DOI: 10.1016/J.TET.2016.10.009

[34] Mandal D, Mandal SK, Ghosh M, et al. Phenylboronic acid appended pyrene-based low-molecular-weight injectable hydrogel: Glucose-stimulated insulin release. Chemistry—A European Journal. 2015;**21**:12042-12052. DOI: 10.1002/chem.201501170

[35] Zhao Y, Zhou L, Liu J, et al. Preparation and investigation of a novel levobupivacaine in situ implant gel for prolonged local anesthetics.

Artificial Cells, Blood Substitutes, and Biotechnology. 2017;**45**:404-408. DOI: 10.3109/21691401.2016.1160406

[36] Hu B, Wang W, Wang Y, et al. Degradation of glutamate-based organogels for biodegradable implants: In vitro study and in vivo observation. Materials Science and Engineering: C. 2018;**82**:80-90. DOI: 10.1208/s12249-018-1074-4

[37] Long D, Gong T, Zhang Z, et al. Preparation and evaluation of a phospholipid-based injectable gel for the long term delivery of leuprolide acetaterrh. Acta Pharmaceutica Sinica B. 2016;**6**:329-335. DOI: 10.1016/j.apsb.2016.05.004

[38] Martin B, Brouillet F, Franceschi S, et al. Evaluation of organogel nanoparticles as drug delivery system for lipophilic compounds. AAPS PharmSciTech. 2017;**18**:1261-1269. DOI: 10.1208/s12249-016-0587-y

[39] Pernetti M, Vanmalssen K, Kalnin D, et al. Structuring edible oil with lecithin and sorbitan tri-stearate. Food Hydrocolloids. 2007;**21**:855-861. DOI: 10.1016/j.foodhyd.2006.10.023

[40] Lupi FR, Greco V, Baldino N, et al. The effects of intermolecular interactions on the physical properties of organogels in edible oils. Journal of Colloid and Interface Science. 2016;**483**:154-164. DOI: 10.1016/j.jcis.2016.08.009

[41] Huang CB, Chen LJ, Huang J, et al. A novel pyrene-containing fluorescent organogel derived from a quinoline-based fluorescent porbe: Synthesis, sensing properties, and its aggregation behavior. RSC Advances. 2014;**4**:19538-19549. DOI: 10.1039/c4ra02373k

[42] Pirner D, Dulle MEJ, Mauer M, et al. Reinforcement of nanostructured organogels by hydrogen bonds. RSC Advances. 2016;**6**:42730-42738. DOI: 10.1039/c6ra03567a

[43] Simsolo EE, Eroglu I, Tanriverdi ST, et al. Formulation and evaluation of organogels containing hyaluronan microparticles for topical delivery of caffeine. AAPS PharmSciTech. 2018;**19**:1367-1376. DOI: 10.1208/s12249-018-0955-x

[44] Steed JW. Supramolecular gel chemistry: Developments over the last decade. Chemical Communications. 2011;**47**:1379-1383. DOI: 10.1039/c0cc03293j

[45] Yu X, Chen L, Zhang M, et al. Low-molecular-mass gels responding to ultrasound and mechanical stress: Towards self-healing materials. Chemical Society Reviews. 2014;**43**:5346-5371. DOI: 10.1039/c4cs00066h

[46] Co ED, Marangoni AG. Organogels: An alternative edible oil-structuring method. Journal of the American Oil Chemists' Society. 2012;**89**:749-780. DOI: 10.1007/s11746-012-2049-3

[47] Hu B, Sun W, Yang B, et al. Application of solvent parameters for predicting organogel formation. AAPS PharmSciTech. 2018;**19**:2288-2300. DOI: 10.1208/s12249-018-1074-4

[48] Hoffmann H. Fascinating phenomena in surfactant chemistry. Advances in Colloid and Interface Science. 1990;**32**:123-150. DOI: 10.1016/0001-8686(90)80015-R

[49] Gennes PG. Scaling Concepts in Polymer Physics. London: Cornell University Press; 1979

[50] Gelbart WM, Ben-Shaul A. The 'new' science of 'complex fluids. The Journal of Physical Chemistry. 1996;**100**:13169-13189. DOI: 10.1021/jp9606570

[51] Sonin AS, Churochkina NA. Liquid crystals stabilized by physical networks.

Polymer Science, Series A. 2013;**55**:353-384. DOI: 10.1134/S0965545X13060060

[52] Hirst AR, Smith DK, Harrington JP. Unique nanoscale morphologies underpinning organic gel-phase materials. Chemistry—A European Journal. 2005;**11**:6552-6559. DOI: 10.1002/chem.200500501

[53] Wu S, Gao J, Emge TJ, et al. Solvent-induced polymorphic nanoscale transitions for 12-hydroxyoctadecanoic acid molecular gels. Crystal Growth and Design. 2013;**13**:1360-1366. DOI: 10.1021/cg400124e

[54] Imai M, Hashizaki K, Taguchi H, et al. A new reverse worm-like micellar system from a lecithin, multivalent carboxylic acid and oil mixture. Journal of Colloid and Interface Science. 2013;**403**:77-83. DOI: 10.1016/j.jcis.2013.04.033

[55] Nikiforidis CV, Scholten E. Self-assemblies of lecithin and α-tocopherol as gelators of lipid material. RSC Advances. 2014;**4**:2466-2473. DOI: 10.1039/c3ra46584e

[56] Lan Y, Corradini MG, Weiss RG, et al. To gel or not to gel: Correlating molecular gelation with solvent parameters. Chemical Society Reviews. 2015;**44**:6035-6058. DOI: 10.1039/C5CS00136F

[57] Haldar S, Karmakar K. A systematic understanding of gelation self-assembly: Solvophobically assisted supramolecular gelation via conformational reorientation across amide functionality on a hydrophobically modulated dipeptide based ambidextrous gelator, N-n-acyl-(l)Val-X(OBn). RSC Advances. 2015;**5**:66339-66354. DOI: 10.1039/c5ra10209j

[58] Zhao C, Wang H, Bai B, et al. Organogels from unsymmetrical π-conjugated 1,3,4-oxadiazole derivatives. New Journal of Chemistry. 2013;**37**:1454-1460. DOI: 10.1039/c3nj40648b

[59] Edwards W, Smith DK. Dynamic evolving two-component supramolecular gels-hierarchical control over component selection in complex mixtures. Journal of the American Chemical Society. 2013;**135**:5911-5920. DOI: 10.1021/ja4017107

[60] Bustamante P, Navarro-Lupión J, Peña MA, et al. Hildebrand solubility parameter to predict drug release from hydroxypropyl methylcellulose gels. International Journal of Pharmaceutics. 2011;**414**:125-130. DOI: 10.1016/j.ijpharm.2011.05.011

[61] Bonnet J, Suissa G, Raynal M, et al. Organogel formation rationalized by Hansen solubility parameters: Dos and don'ts. Soft Matter. 2014;**10**:3154-3160. DOI: 10.1039/c4sm00244j

[62] Bonnet J, Suissa G, Raynal M, et al. Organogel formation rationalized by Hansen solubility parameters: Influence of gelator structure. Soft Matter. 2015;**11**:2308-2312. DOI: 10.1039/c5sm00017c

[63] Trickett K, Eastoe J. Surfactant-based gels. Advances in Colloid and Interface Science. 2008;**144**:66-74. DOI: 10.1016/j.cis.2008.08.009

[64] Israelachvili J. Intermolecular and Surface Forces. 3rd ed. USA: Elsevier; 2011

[65] Suzuki M, Hanabusa K. Polymer organogelators that make supramolecular organogels through physical cross-linking and self-assembly. Chemical Society Reviews. 2010;**39**:455-463. DOI: 10.1039/b910604a

[66] Dastidar P. Supramolecular gelling agents: Can they be designed? Chemical Society Reviews. 2008;**37**:2699-2715. DOI: 10.1039/b807346e

[67] Zhang Z, Zhang S, Zhang J, et al. Solvent-dependent self-assembly and morphological transition of

low-molecular-weight azobenzene organogel. Tetrahedron. 2017;**73**: 4891-4895. DOI: 10.1016/j.tet.2017.05.027

[68] Sahoo S, Kumar N, Bhattacharya C, et al. Organogels: Properties and applications in drug delivery. Designed Monomers and Polymers. 2011;**14**: 95-108. DOI: 10.1163/138577211X555721

[69] Daniel J, Rajasekharan R. Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids. Journal of the American Oil Chemists' Society. 2003;**80**:417-421. DOI: 10.1007/s11746-003-0714-0