# Oleogels and Their Contribution in the Production of Healthier Food Products: The Fats of the Future

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**Abstract**   Consumption of animal fats, calorie-dense and simple carbohydrate-rich diets along with a more sedentary life style have triggered the outcome of cardiovascular and obesity disorders. A worthy alternative is to replace these of saturated fats with healthier ingredients in a texturized oleogel. Oleogelation promises to decrease the incorporation of harmful fats granting good mechanical properties to food products by creating crystalline colloidal networks upon contact with a gelator. Thus, unsaturated fatty acids from oils are thus trapped and retained forming gels having microscopic self-assembled crystalline particles of different shapes. Currently, most oleogels have been developed with vegetable oils by applying gelators such as polymers, partial glycerides, waxes and fatty acids improving the mechanical and thermal properties of food products. This review is focused on the progress regarding oleogelation and the physical interactions responsible for the intermolecular conformation, physical properties, additives and microstructure required for the substitution of harmful saturated and *trans* fats. Likewise, the most recent advances, regarding their potential functionality and applications as the fats of the future are also discussed.

*Keywords: food texturing, gelators, oil migration, oleogels, vegetable oils*

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## 1. Introduction

The lack of good eating habits has turned people attention toward the consumption of foods with a high caloric content (i.e., saturated and *trans* fats) generating an immediate satiety, but causing long term multiple disorders due to the accumulation of fat in the human body [1]. In fact, diets rich in saturated and *trans* fatty acids cause arterial injuries due to their accumulation as platelets on the walls of the arteries, releasing thrombi in the cardiovascular system triggering diverse metabolic disorders [2]. The World Health Organization recommends a daily intake between 15 and 30% with a maximum saturated fatty acids intake of 10% [3]. Besides the nutritional value, saturated fats also ensure the sensory and texture quality of food products in confectionery, meat, bakery, and other products. Thus, saturated fats are crucial for generating plastic textures controlling the viscosity of the food products [4]. For instance, in the bakery industry they are responsible for providing adhesion between starch granules and gluten improving lubrication, and forming smoother particles of uniform shapes [5]. In fact, saturated fats are essential, since they (i) provide mechanical qualities (ii) render better taste perceptions on the palate, (iii) contribute to the gelatinization of starch, and (iv) ease the formation of complexes between amylose and fatty acids. Therefore, they play a fundamental role in the sensory and life-span quality of food products [6].

Typically, the reduction of fats in processed foods would bring technological problems such as a decrease in the texture and adverse changes on the rheological properties which are translated in a reduction of the typical flavors and odors awarded by the fatty substances [7]. In addition, saturated fatty acids ease the transformation phenomena during cooking of fried foods. Thus, the oxidation resistance is prolonged and stabilized, whereas the opposite effect occurs when unsaturated fatty acids are used at frying, causing greater susceptibility to oxidation [8]. Further, saturated fatty acids affect the juiciness, texture and guarantee the structure and stability of processed foods [9]. For instance, the emulsifying capacity of agents such as pork fat allows for the crystallization of fats building texture and thixotropy [10]. Conventionally, several strategies have been conducted to replace saturated fats converting liquid oils to semisolids changing the molecular configuration through hydrogenation, interesterification, and fractionation processes. Particularly, the possible formation of *trans* fats upon hydrogenation precludes their use since they are associated with cardiovascular diseases [11]. The melting point of fats increases with saturation and isomerization, whereas cooling below this point eases

crystallization and hence gelation of the material [12]. Thus, a saturated fat in a food product will prevent the exudation of oil during storage in a packed product. Even though such saturated and *trans* fats possess constructive benefits on the sensory, stability and textural characteristics of food products, their long term consumption might cause several metabolic disorders. Oleogelation could resolve this issue by structuring liquid oils with low levels of gelators allowing for the formation of a semisolid material [13]. Thus, oleogels are used to (i) prevent the loss of oils in products already packaged, (ii) protect and control the release of hydrophobic bioactive compounds, (iii) trap organic solvents, (iv) award longer shelf-life and (v) provide strong rheological characteristics despite of having a mainly liquid composition [12]. Therefore, this review highlights the new developments that guarantee liquid oils structuring through oleogelation in order to replace saturated and *trans* fatty acids with optimal, stable and healthier compounds in food matrices. Moreover, a description of innovative oleogelation strategies, gelators and vegetable oils involved is also debated.

## 2. Structuring Methods for Oleogelation

Oil structuring could be carried out by two methods. The direct method is based on the process of reorganization of the gelators once surpassed the glass transition or melting point. This reorganization physically traps the oil changing the physicochemical properties. Conversely, indirect methods involve techniques such as solvent exchange and emulsification. For instance, the latter consists of an O/W emulsion or aqueous foam template in which that polymers such as hydroxypropylmethyl cellulose (HPMC) and methyl cellulose (MC) absorb at the interface. Subsequently, freeze-drying is carried out to eliminate the continuous aqueous phase of the primary emulsion leading to the formation of a fine polyhedral network which can trap a very high amount of oil (~ 99%). These polymers create a colloid in the air/water interface stabilizing a hydrophilic foam (at low temperatures) by forming a porous template with a high affinity with oil forming gels once water has been eliminated from the system. The dried product is then dispersed in liquid oil

and, therefore, the polymer sheets can be joined and liquid oil is incorporated forming a polymeric gel.

## 3. Oil-gelator Interaction Forces

Several forces such as dispersive, polar and hydrogen bonds govern oil-gelator miscibility and hence the likelihood of crystal formation and ~~hence~~ gelation. Therefore, all these variables affect the rheological behavior, along with the chain length of fatty compounds which change the spatial orientation of crystals, affecting the strength of the resulting oleogel [14]. Thus, the gel texture tends to be lost as the interactions between the gelator and oil components are eased since solubilization rather than the self-assembly of crystal components is favored. Therefore, oil polarity affects the magnitude of self-assembling since oils having low polarities assemble into short and dispersed fibers which grow and become interconnected, whereas oils with high polarity form conglomerates due to the free mobility in the medium. For instance, oleogels created with ricinoleic acid showed a gelation rate decrease when more hydrogen bonds are formed [15]. Conversely, oleogels made from polymers such as ethyl cellulose (EC) are highly strong if the oil polarity increases [16]. Further, the gelling capacity is conditioned by the forces between the insoluble and soluble components of the gelator and the oil. Therefore, the gelling molecules should be partially insoluble with the oil to encourage crystallization or self-assembly (gelling-gelling), but at the same time should have a partial solubility within the oil phase to generate polar and hydrogen bond interactions [17]. Thus, an apparent balance between hydrogen bonds and hydrophobic interactions become a critical factor that eases self-assembling and the formation of a defined nano/micro architecture [18]. Other interactions might include dipole-dipole and induced dipole-dipole forces [19]. Strong oleogels with polymers reveals long and thin interconnected fibers mainly through hydrogen bonds. Conversely, weak gels exhibit thick and rigid fibers interconnected by Van der Waals forces resulting in aggregation (Figure 1). Further, an excess in the gelator causes a supersaturation of the oil phase changing the directional fiber growth leading to the creation of thick fibers [20].
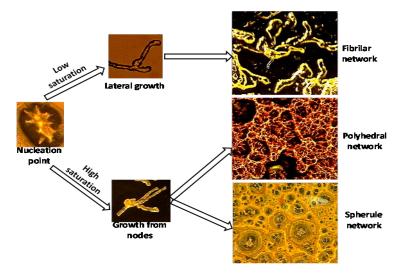


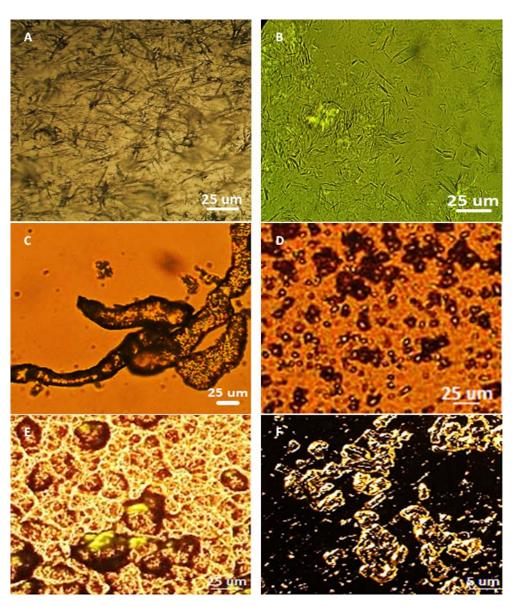**Figure 1.** Schematic representation of crystal growth

**Figure 2.** Classification of oleogels. (A) Self-assembling with low molecular weight gelators, (B) Crystalline particles, (C) Polymeric agents with hydroxyl ethyl cellulose (D) Miscellaneous (emulsion), (E) Miscellaneous (dispersion), (F) miscellaneous (inorganic particles)

# 4. Classification of the Supramolecular Assemblies

Gels are classified as hydrogels and organogels (oleogels), whether the solvent is hydrophilic or hydrophobic, respectively [21]. They are also classified according to the gelator molecular weight into low molecular weight and polymeric gelators. However, the most common classification is given in terms of the type of the resulting supramolecular assembly (building blocks) [22] of the crystals observer under the microscope (Figure 2).

## 4.1. Self-assembling with Low Molecular Weight Gelators (SAFIN)

SAFIN develop crystalline and elongated particles that might reach hundreds of micrometers in size [23]. This group involves gelators such as, fatty alcohols, glycerols, sorbitan esters, fatty acids, cholesterol, lecithin, phospholipids, sphingolipids, ceramides, and oils such as

D-limonene, γ-oryzanol, β-phytosterol, tocopherols and ricinoleic acid [24]. These compounds are able to form oleogels since they dissolve at high temperatures and upon cooling crystalline particles are aggregated into elongated particles linked by several types of interactions [25]. These crystalline particles are formed by nucleation and further crystalline growth in the oil phase. Usually, crystallization occurs after reaching certain level promoting structuring upon cooling. Particle crystallization could self-assemble into either non-crystalline particles such tubules, fibers or inverse micelles [26]. For instance, the fiber-like shape is created by unidirectional crystal growth originated from a single nucleation point resulting in a 3D fibrillary network as occur for hydroxylated fatty acids [22]. The gelling capacity improves with increasing chain length and, therefore, non-polar compounds with a chain length larger than $C_{18}$ could gel oils at levels as low as 2%. Likewise, highly unsaturated oils could form a more dense gel network, whereas viscous and polar oils tend to form oleogels with a lower strength. In turn, the amount of oil trapped within the gel depends on the magnitude and type of interaction forces between the crystalline particles

formed [27]. Some of these gels are transparent and show birefringence when observed under polarized light [28]. Further, as the content of gelator increases the gel transparency decreases [29,30].

## 4.2. Crystalline Particles

Waxes are highly effective gelators having a very low gelling level and a high oil retention capacity [22]. Their good crystallization is due to their low polarity and very long chain length exhibiting also a high melting point [31]. Oleogels based on triacyl glycerol, diacyl glycerol, monoacyl glycerol, or beewax, rice wax, candelilla wax, carnauba wax among others, tend to create needle-shaped crystals with sizes ranging between 10 and 25 μm at very low levels (1.0% w/w) [32]. Since waxes are composed by linear molecular structures such as esters, fatty acids, fatty alcohols and hydrocarbons they form crystals that grow predominantly in a two-dimensional space (slight lateral growth) [33]. Further, they are thermo-reversible in nature allowing for a transition of the material in gel-solid state as a function of temperature. Further, waxes act as emulsifiers due to the surfactant action generated by their fatty alcohols which in turn, stabilize the interface due to the accumulation of crystalline particles [22]. It has also been found a relationship between the crystal shape and texture [17]. Further, if crystals are reorganized as occurs in candelilla wax, they are able to refract polarized light in several directions [34].

## 4.3. Polymeric Agents

They are produced with hydrophobic polymers (i.e., EC) [35], polysaccharides (chitosan and chitin) [36] and macromolecules such as lactoglobulins [37] and zein [38]. This assembling involves self-organization in the oil phases. In fact, gelation with polymers is achieved by self-assembly generating polymeric fibers. Hydrophobic polymers promote gelation in two ways: (i) by forming chemical gels through covalent bonds and (ii) forming physical gels by self-assembling via hydrogen or van der Waals forces (physical gels) [39]. For instance, EC is a hydrophobic cellulose that generates oleogels upon dispersion in the oil phase followed by heating above the Tg (130 °C). Subsequently, the polymer chains unfold and upon cooling at low temperatures, chain entanglement by hydrogen bonds occurs between the polymer chains. EC also possess thermoreversible properties in the solid-gel transition [40].

## 4.4. Miscellaneous

This group comprises the particle-filled networks and liquid crystalline mesophases. The former implies the injection of a solid or liquid filler in the continuous lipid phase. As a result, a thick dispersion or emulsion is obtained. For instance, materials such as fumed silica become entangled forming a 3D network which traps oils such as sunflower oil [22]. The second group implies the formation of semicrystalline scaffolds in the oil with gel-like properties. In this case, lyotropic liquid crystals are used as fat replacers and consist of cylinders filled with hydrophilic liquids such as polyols.

## 5. Factors that Affect Oleogelation

The growth and morphology of the crystals is affected by the amount and combination of gelators, cooling rate, crystallization temperature [41], intensity of ultrasound or microwave [42], treatment pressure [43] and stirring rate [44]. Self-forming fibers are the result of the process of nucleation and branched growth under cooling [28]. In turn, this process depends on the degree of saturation of the medium. Therefore, a low saturation degree promotes a high disorder of the crystals, favoring growth and entanglement of fibers without branching. Conversely, a high degree of saturation promotes an interfacial structural disorder causing growth without optimal orientations, leading to massive ramifications interrupted by fibrillar chaos, resulting in short and thin branches that emerge from the tip of the crystal and grow as spherulites [45].

## 5.1. Oil Type

The oil polarity, heating temperature, external shear and addition of surfactant could affect the final gel properties, since they affect the strength of hydrogen bonds. For instance, soft EC gels are obtained at a very low setting temperature due to a fast and chaotic chain association as compared to those obtained at a higher setting temperature. This is explained by the high energy of the system causing a stretched state of the polymer due to massive hydrogen bond formation leading to greater entanglement and more interpolymer bonding zones. Further, a high unsaturation degree of the oil induces a greater freedom of conformation and a greater molar volume resulting in a twisted spatial arrangement, decreasing the interaction energy. This, in turn, leads to a more hydrophobic oil behavior forming more bonding points resulting in stronger gels [46]. For instance, a high polarity of the oil leads to greater gel strength since the oil phase polar groups easily interact within the EC network. In addition, by increasing the oil polarity the strength of hydrogen bonds in the gelator decreases affecting the thermal stability of the gel [47]. Conversely, the incorporation of polar co-solvents such as ethanol stimulates the gel toward a microcrystals transition [48].

The length of the triglyceride carbon chain and its saturation degree influences the way in which the gelator generates the 3D network. For instance, low molecular weight solvents such as acetone, ethyl acetate, hexane and oil form clear EC gels. In addition, solvents having an opaque nature generate oleogels that do not maintain their structure over time. Conversely, solvents such as acetone and toluene form a chaotic network of microfibers [16].

The saturation and unsaturation degree of the oils also affects the minimum gelling level and a lower gelation level occurs when the oil contains high levels of saturated fats. This phenomenon is explained by (i) the higher melting temperature and, therefore, the resulting high strength of the oleogel, (ii) a low melting implies a depletion of the solubility of the oil forming a highly crystalline network with the gelator. For instance, a minimum gelling level of beeswax is very low in rice bran oil containing a higher saturation degree as compared to rape seed oil containing a higher unsaturation degree. Further, strong oleogels are obtained when using oils

containing long chain saturated fatty acids. In addition, oils also influence the pore diameter of the oleogel. This diameter decreased with increasing unsaturation degree of the fatty acids present in the oil. Further, the oil type influences the rigidity of the gels. Thus, oils rich in unsaturated fatty acids produce stronger gels. For instance, linseed, canola and soybean oils, containing >50% linoleic (18:2), oleic (18:1) and linolenic (18:3) acids, respectively formed strong gels. Therefore, a larger unsaturation degree eases the formation of a greater number of interpolymer bonding points [49].

Further the oxidation degree of the oil also affects gelation. Thus, a high oxidation degree increases the oil polarity increasing the mechanical strength of the gel [46]. For instance, the polarity of soybean oil increases by adding castor oil, resulting in an extended open chain configuration leading to a greater number of gelator-gelator interactions and hence better gel strength [16].

## 5.2. Gelator Type

### 5.2.1. Sugar Esters and Acyl Glycerides

Sugar esters show an amphiphilic nature so they are capable of self-assembly via Van der Waals and hydrogen bond forces at levels ranging from 2 to 20%. Sorbitans are non-ionic surfactants capable of gelling oils forming thermorevesible and opaque gels. Sorbitan esters promote the formation of W/O emulsions and tubular structures upon crystallization. Their gels are opaque and thermo-reversible having a minimum gelation level of 10% [50]. On the other hand, glycerol monoesterate (GM) and triestearate (GT) have a hydrophilic head and hydrophobic tails of different length ($C_{8-10}$ or $C_{16-18}$). GM forms needle-like crystals in olive oil, whereas it forms spherulite-like crystals in corn oil. Typically, the hydrophilic head of sorbitan would produce more compact structures as compared to those having glycerol heads, although the hydrophobic head implies a compact gelation exhibiting birefringence [51].

At low levels (5% w/w), GM shows self-assembly gels, whereas SM, ST, GT exhibit a semifluid behavior [25]. In addition, GM shows higher elastic component (G') as compared to SM and ST since the hydrophilic head of glycerol is smaller and less heavy as compared to that of sorbitan. Moreover, sorbitan has a ring attached to a carbonyl group, which offers more rigidity to the structural network. Therefore, a smaller voluminous conformation allows molecules for creating hydrophobic, dipole and hydrogen bonding forces resulting in a strong and elastic gel resistant to deformation [52]. In general, the longer the carbon chains of the fatty alcohols used the smaller and thinner crystals are formed. They produce oleogels containing needle-shaped crystals and lamellar structures regardless of the length of the chain [53].

### 5.2.2. Lecithin

Lecithin is capable of forming inverse spherical micelles when it dissolves in oils and subsequently entangle, forming a 3D gel network. These micelles are responsible for the immobilization of the continuous oil phase and facilitate the formation of a strong gel.

Further, the addition of polar solvents such as water promotes unilateral growth of the reverse micelles forming cylindrical or tubular aggregates having a diameter from 4 to 5 nm and a length from 100 to 1000 nm resulting in a stronger gel having high oil entrapment efficiency [54].

### 5.2.3. Ceramides

Ceramides are composed by a fatty acid attached to an amino group of sphingosine. They can form lipid gels with oils at levels as low as 2% and this level increases as the fatty acid length increases. Ceramides having a high fatty acid content form gels containing long and thin fibrillar crystals, whereas heterogeneous ceramides create gels containing essentially spherulite-shaped crystals [55].

### 5.2.4. β-Phytosterol and γ-oryzanol

γ-oryzanol is a compound found in rice bran oil at high levels (1-2%) whereas, β-phytosterol is found in numerous vegetable oils. They form transparent gels with a fibrilar structure due to the molecular stacking between γ-oryzanol and β-phytosterol. This property also depends on the relationship between these two components since once melted the solution goes through a super saturation and then cooled, leading to phase separation and nucleation promoting crystal growth in one dimension forming helical ribbons, twisted tubules and fibers. Oleogels that have 5-10% levels of β-phytosterol and γ-oryzanol are very firm, but slippery due to the presence of hydroxyl groups which limit solubility, and hence during the cooling stage alignment of hydroxyl groups and reduction of the contact points with the solvent occurs [22]. Gels are produced thanks to the C-3 hydroxyl group of phytosterol and must have less than two double bonds in the stearane ring. The C-3 OH allows for the formation of hydrogen bond between γ-oryzanol and β-phytosterol. These bonds stabilize the stacking of the two components by minimizing free energy. This stacking is slightly embedded, forming helical tubules. The nuclei of both compounds form a wall of fibers whose thickness depends on the size of the sterol nucleus. Typically, the thickness and diameter of the wall ranges from 0.8 to 1.2 nm and from 6.7 to 8.0 nm, respectively, depending on the sterol nucleus [56].

### 5.2.5. 12-Hydroxystearic Acid (12-HSA).

It forms thermo-reversible oleogels by heating above the melting point (~76 °C). Upon cooling, the hydroxyl groups form hydrogen bonds easing the growth of brittle fibers in one dimension. These fibers break under mixing or shearing, resulting in a high oil loss. Further, high cooling rates (>5°C/min) result in the development of shorter fibers, whereas slower rates create long fibers [32] [57]. On the other hand, ricinoleic and ricinoleidic acids gel similarly to 12-HSA. In fact, the dimers stack forming a fibrilar 3D network structure with gelator levels as low as 2.5% and 4% in canola and sesame oils, respectively. However, upon storage, these gels may show changes in crystallinity affecting their stability [52]. Further, the 12-HSA and ricinoleic acids, form ellipsoidal structures and twisted crystalline ribbons due to the unidirectional growth of the crystals resulting in short strands [22].
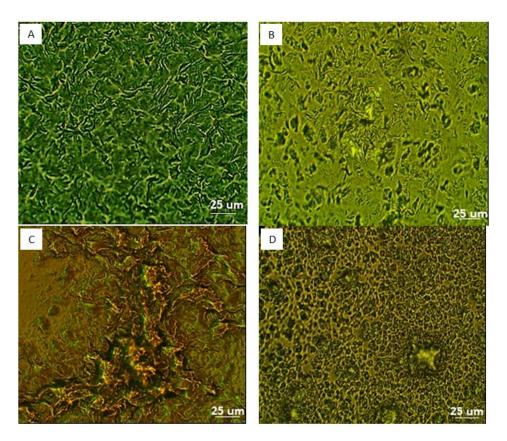
**Figure 3.** Phase contrast microphotographs of oleogels prepared with Beewax (A), candelilla wax (B), ozokerite wax (C) and carnauba wax (D)

**Table 1. Chemical composition of some natural waxes used as gelators**

| Wax | Component | Amount (%) |
|---|---|---|
| Candellila | Nonacosane ($C_{29}$) | 49% |
| | Tritriacontane ($C_{32}$) | 50% |
| | Esters | 20-29% |
| | Free acids | 7-9% |
| | Resins | 12-14% |
| | Wax esters $C_{38}$-$C_{54}$ | 66-69% |
| Sunflower | Fatty acids | 12-16% |
| | Fatty alcohols | 11-13% |
| | Hydrocarbons | 6-7% |
| | Wax esters | 38-40%, |
| | P-hydroxycinnamic aliphatic diesters | 20-23% |
| Carnauba | Monohydric alcohols | 10-12% |
| | X-hydroxy esters | 12-14% |
| | P-methoxycinnamic aliphatic diesters | 5-7% |
| | Wax esters $C_{44}$-$C_{64}$ | NR |
| Rice Bran | Fatty acids $C_{24}$ | NR |
| | Aliphatic alcohols | NR |
| | Monohydric alcohol $C_{24}$ to $C_{36}$ | NR |
| | Fatty acids $C_{50}$ | 35% |
| | Hydroxyl esters (mainly ester of 15-hydroxypalmitic acid and $C_{24}$-$C_{34}$ alcohols) | 24% |
| | Hydrocarbons | 14% |
| | Diesters | 12% |
| Beeswax | Free acids | 12% |
| | Unidentified compounds | 6% |

## 5.2.6. Natural Waxes and Resins

Waxes are composed by hydrocarbons, long chain esters, phytosterols, fatty acids, fatty alcohols and their composition varies according to their source (Table 1). They possess a high gelling efficiency (0.5-7% w/w) due to their high content of high molecular weight esters (20 and 29%) forming a crystalline platelet morphology, especially for sunflower, candelilla and carnauba waxes [29]. Candellila wax forms thermo-reversible oleogels with safflower oils at levels as low as 2% exhibiting crystalline spheres of less than 10 µm in size. In addition, their oil retention capacity depends on the level of wax [58]. For instance, candelilla wax showed a sunflower oil loss of 25.8% at 1% level, whereas at 2% level it lost 11.1% oil [30]. Further, crystal morphology is affected by the type of wax and oil employed. For instance, candelilla

wax generates fine crystals between 3 and 5 μm in size (Figure 3). Conversely, rice bran wax generates oleogels having crystalline needles from 10 to 50 μm in length at levels ≤1.0% maintaining a gel microstructure with good viscoelastic properties [59]. In another study, wax of rice germ, sunflower and candelilla at 2.0% level were mixed with peanut oil, originating crystalline platelets, whereas the same waxes combined with olive oil formed needle-shaped crystals [60]. Beeswax has a sea urchin shape structure due to the two-steps crystallization process: (i) the formation of 3D spherulites, followed by a (ii) nucleation of needles from the center of the microparticle with a lateral growth [61]. Other studies of beeswax in rice germ oil generated a crystalline morphology in form of spherulites [62]. These spherules were also observed in oleogels prepared from sunflower oil with beeswax (0.5% w/w) [63]. However, when canola and soybean oils are used with beeswax, the crystals acquire an irregular shape [64]. These morphologies are constant even when sonication is applied as long as canola oil is used. On the contrary, crystalline forms are not observed when soybean and sunflower oil are treated with sonication. On the other hand, carnauba wax has a melting temperature of 84°C. It has a low gelation level (4%) and a gelation time of 13.5 minutes at 25°C. Carnauba wax forms 3D rod-like crystals of <10 μm in size which are essential for self-assembly and immobilization of a large quantity of oil creating large aggregates (50-100 μm) [17]. This wax exhibits the lowest strength as compared to other waxes when gelling hazel nut oil. Likewise, shellac is a wax which creates thermo-reversible emulsions and firm oleogels which are applied in cake products [62].

### 5.2.7. Polymer Oleogels

They perform oil structuring by forming a 3D network by physical or chemical crosslinking between the polymer chains (Figure 4). The gel strength depends on the polymer molecular weight and their degree of crosslinking. Polymer oleogels also offer an advantage over other gelators such as triacyl glycerol (TAG) since their oleogels are stable to molecular rearrangement and thermoreversible, whereas TAG recrystallizes upon storage. They form physical gels characterized by the formation of non-covalent binding points of different size, number, and position depending of the processing conditions. These systems never reach a state of final equilibrium due to the formation of secondary chains, reorganization, stacking or rupture of the already formed binding points. The main physical interactions in polymer gels involve hydrogen bonds, dipole-dipole and hydrophobic forces forming a secondary structure (i.e., helices, double helices or crystals). For instance, agarose and gellan gum gels have a conformational transition from coil-helix followed by helix-helix. Conversely, κ-carrageenan is gelatinized by a transition from a double-helical conformation promoting the creation of supramolecular aggregates [65]. The addition of ions acting as crosslinkers induces gelation in polymers such as alginate and pectin [66]. Methylcellulose (MC) is a cellulose derivative that, when heated forms gels by hydrophobic forces [67]. On the other hand, HPMC is able to form hydrophobic interactions when heated forming tiny micelles [68]. A remarkable polymer is EC due to its ability to form oleogels directly. The commercial EC has an ethoxy substitution degree of 2.5 (47-48% ethoxy content). It is water insoluble, but soluble in oil upon heating. EC should be heated above its Tg (120-135 °C) in order to form gels. Further, its melting point ranges from 165 to 173 °C. However, the exact transition temperature depends on its molecular weight [69]. In fact, the glass transition, crystallization and gel point increase with the increase in molecular weight, which in turn is reflected on the formation of stronger gels [35]. Therefore, longer chains form greater number of junction zones forming a stronger gel network. EC unfolds upon reaching the Tg leading to partial solubilization in the oil, followed by cooling inducing the formation of interpolymer hydrogen bonds. Thus, a physical gel is shaped by the magnitude of hydrogen bonds between the unsubstituted hydroxyl groups of the ethoxylated glucose units and type of oil. It gels soybean and canola oils at levels of 4% and 6%, respectively, whereas gelation of propylene glycol dicaprylate with EC requires 11 and 7% levels, respectively. Further, the increase in EC from 10 to 14% decreases the pore size from ~4.5 to 3 nm. Heating of EC oleogels shows a decrease in gel strength suggesting breakage of hydrogen bonds and destabilization of the polymer lattice. Therefore, a high gel structuring occurs when the melted gel is heated above the melting temperature of the polymer. Particularity, the polymer network can also rearrange upon gelation changing the gel strength resulting in good storage stability for 90 days at room temperature [35].
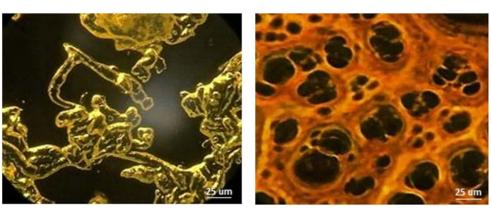


**Figure 4.** Polymeric strands (hydroxyethyl cellulose)

# 6. Several-component Oleogel Systems

The use of a single type of oil guarantees gelation of the system through one type of interactions, such as hydrogen bonds. However, when two components are incorporated (oil or gelator), one of them tends to interact more with the other components generating aggregates that subsequently form a 3D gel network [70]. The combination of two gelators provides a synergistic effect for gelation resulting in a gel having a different microstructure, since these molecules self-assemble uniformly in different conformations, creating dense networks. For instance, a combination of fatty alcohols (n=16-22) and fatty acids (n=16-20) renders stronger gels than the individual components. In addition, the gel strength depends on the fraction of the two structuring components which in turn determine the self-assembly type. Sorbitan tristearate (ST) has been added to lecithin promoting crystallization when both components have equal levels. The mixture of ST and lecithin at a 40:60 and 60:40 ratios produce thermo-reversible gels at levels as low as 6% having a needle-shaped or platelet-shaped crystals of ~10 μm in length. Another example is the combination of 15% lecithin with α-tocopherol creating reverse micellar structures. The retention efficiency of the oil is also improved by combining stearyl alcohol and stearic acid forming stronger oleogels upon cooling [71].

Surfactants, such as glycerol, can interact and bind to the gelator acting as plasticizer. They reduce the Tg of the solid-gel and the gel-solid phase transition facilitating the penetration force of the oleogels, resulting in a higher gel strength [40]. In another study, EC oleogels prepared in a stearic alcohol and stearic acid mixture create a plasticizing effect [16]. Moreover, surfactants reduce the crystallization temperature and enthalpy of the gelator. Therefore, at low temperature (90 °C) G' has a greater extent than G", whereas at high temperature (140 °C), the magnitude of these modules is reversed. This behavior is due to the plasticizing effect of glycerol as compared to the main group of sorbitan surfactants. Further, surfactants allow for a rapid recovery of viscosity of gels submitted to fixed shear. Conversely, EC gels having no surfactants are not able to recover their structure upon shearing [72].

On the other hand, the combined effect of sterols and phytosterols creates self-assembled helical ribbon structures linked by hydrogen bonds between carbonyl moieties of oryzanol and hydroxyl group of phytosterol [56]. Usually, monoglycerides form unstable gels with granular crystals, whereas phytosterols crystallize in form of long flattened crystals, generating weak oleogels. However, a 10% mixture of monoglycerides and phytosterols forms oleogels having better rheological properties and long shelf-life [22]. However, the incorporation of large amounts of phytosterols hinders interactions with monoglycerides [73]. The mixture of surfactants derived from sucrose esters and lecithin forms atypical oleogels. This is explained by the small (≤10 μm) spherical or globular crystals of sucrose esters in sunflower oil, which form heterogeneous aggregates which do not contribute to the formation of the gel [74].

Likewise, a mixture of sesame oil, sucrose monosorbate, and silicone causes a reduced solubility of the gelator in the oil, resulting in self-assembly of the molecules in form of tubular vesicles. Silicone also causes a reduction in viscosity, due to alteration of the solvent polarity changing the number of hydrogen bond interactions [75].

# 7. Oleogels in Food Applications

Solid lipids are commonly used in industrial products such as patty, pasta and cake due to their good oxidative stability and provide characteristics such snap, texture, flavor, spreadability and shelf-life. Oleogels are potential substitutes for fats rich in saturated and *trans* fatty acids, emulsion stabilization, restriction of oil migration, and control release of nutraceuticals. The possible applications are described as follows:

## 7.1. Emulsions and Spreads

Some low molecular weight gelators are able to stabilize and structure water-in-oil emulsions due to their amphiphilic nature. Therefore, oleogels can immobilize water droplets within the continuous oil phase. Conversely, the spreads tend to replace the oil phase present in the W/O emulsions, providing the usual consistency and the desired mouthfeel. For instance, shellac creates gels with interesting rheological properties and good properties in spreads, chocolate, pasta and cakes. Likewise, 12-HSA in canola oil having a highly unsaturated profile (30% polyunsaturated and 59% mono fatty acids) has been used as an excellent spread. Starch in mayonnaise has also been used to replace fats which are commonly used at 25, 50 and 75% levels [76]. The G' storage module of starch at 25% and 50% levels was high evidencing a larger structure in mayonnaise, functioning as an emulsifier and decreasing the particle size of fats creating more stability and increasing the elasticity of samples [21]. Further, oleogels dissolved in soybean oils or medium chain triglycerides have been used to stabilize non-aqueous propylene glycol emulsions.

## 7.2. Chocolates

Oleogels provide thermal stability to chocolates stored in countries having a warm climate. Oil migration is the cause of the fat blooming in chocolates. This issue has been addressed with shellac and EC oleogels used as structurants. Since chocolate possesses low molecular weight fats, the incorporation of high melting point oleogels awards better thermal resistance and improve the manufacturing, distribution and consumption of chocolates which are currently produced in a seasonal pattern. For instance, EC is able to form a stable heat resistant chocolate up to 70 °C whereas the control samples melted [77]. This effect is more pronounced in milk and white chocolate which implies a sugar contribution. Thus, the polar groups of EC and sucrose interact via hydrogen bonding structuring chocolate, which in turn is responsible for the thermal resilience [40].

## 7.3. Dough and Pastry

Cookie dough and cake have a high level of saturated fats which are incorporated through butter and cream.

Fats such as lard, butter and margarine are needed to provide the desired mouthfeel characteristics (i.e., by incorporation of air, and moisture barrier) of baked goods. Shortening is an edible fat which prevents cohesion of gluten strands upon mixing rendering a soft texture and mouthfeel to foodstuffs. The fat content in the product prevents the cohesion of the gluten chains. Oleogels produced with olive, soybean and linseed oils and structured with rice bran, sunflower, candelilla and beewax have been used for the manufacturing of cookies. The resulting cookies did not have significant differences in the spreading factor, hardness and brittleness as compared to commercial cookies. Further, oleogels reduce oil migration from dough products. Oleogels prepared from canola oil and candelilla wax are used as a substitute for fat in cookies containing high levels of unsaturated fatty acids. Candellilla wax has been incorporated at the 3 and 6% levels into canola oil resulting in harder biscuits and higher spread ratio. Once the shortening was substituted with oleogel they were harder than products containing shortening. Moreover, the increase in candelilla wax levels enhanced the viscosity of the oleogels, but it decreased upon heating [6]. On the other hand, if only oil is added, baked products become greasier and less crispy and the product shelf-life decreases due to oil oxidation. Further, a low oil viscosity causes a difficult dough handling and shaping. Oleogels made with sunflower oil and beewax are a good substitute for margarine showing a higher waxy taste and a gritty mouthfeel as compared to simple margarine. In another study, an oleogel was added to the wet ingredients of a traditional biscuit recipe and mixed with low-fat Coasun® followed by baking, leading to a reduction in oil migration [72].

## 7.4. Processed Meat Products

The incorporation of oleogels allows for a decrease in fat and cholesterol in pork meat. Oleogels reduce hardness and elasticity. However, cohesion remained unchanged as compared to the pork fat and canola oil controls. Oleogels made from soybean lecithin and monoglycerides showed a slight improvement in stability of the meat sauce due to interactions between oil, lecithin and water, which in turn prevented oil loss. Sterol-based oleogels are good substitutes for pork fat (~50%) in frankfurters, which show no significant physicochemical and sensory differences with commercial products [6]. Oleogels made from canola oil and EC showed a comparable texture as compared to the control sample in terms of chewiness and hardness in Frankfurters. When the oil was structured with EC the fat globules were larger in size as compared to the white globules of meat fat. As a result, the texture of the sausages prepared with the oleogel was similar to sausages prepared with meat fat. In contrast, when pure canola oil was employed a decrease in the oil droplet size was observed [35].

## 7.5. Ice Cream

Oleogels can substitute fats in dairy products such as ice cream since they improve the migration of oils. Thus, the incorporation of emulsified rice bran wax oleogels combined with glycerol monooleate (fat content of 15%) in ice cream results in a big fat globule. For instance, ice creams made with oleogels based on sunflower oil showed similar density and viscosity values, increased melting time and had less over run as compared to regular artisanal ice cream. The ice creams containing oleic oleogels of sunflower exhibited a greater incorporation of air. However, this ice cream showed poorer stability as compared to ice cream prepared with milk fat. On the other hand, HPMC oleogels have been used to prepare cookie cream stabilizing the oil at 50 and 75% fat substitution levels. Another study reports the use of gums to improve the sensory and rheological properties of ice creams. In this case, a 2.5% gum level rendered comparable consistency with gums used at a 10% level. Thus, guar gum and basil seeds generated a high consistency and resistance to shear stresses, as well as a low value of the flow behavior index in ice cream creams having a low fat content [78].

## 7.6. Controlled Release of Nutraceuticals

Oleogels can be employed to improve the solubility and control the release on non-polar compounds since these compounds have a hydrophobic nature. Therefore, the gel network controls the release of the lipids upon contact with the emulsifying enzymes. For instance, canola oil releases β-carotene within 30 minutes, whereas gel-based oils showed full release between 30 and 75 min [79].

# 8. Conclusions and Future Perspectives

Oleogels are used to control the retention and release of oils or liphophilic molecules. Factors such as gelator and oil types, particle size and matrix structure affect the physical gel properties. In turn, the oleogel functionality depends on the composition of oil, gelator level, heating, cooling and gel setting. Gelation occurs mainly by physical interactions such as hydrogen bonding and Van der Waal forces. These interactions are affected by external fields such as shearing and heating. Oleogels can be employed in the manufacture of spreads, margarines, bakery, chocolate and meat products. Thus, they can be used as substitutes for saturated fats in food products. However, much more work will be required to improve their sensory properties and place them on the market.

## Acknowledgements

## References

[1]   Teng KT, Chang CY, Chang LF, et al. Modulation of obesity-induced inflammation by dietary fats: mechanisms and clinical evidence [J]. Nutrition Journal, 2014, 13(1): 12.

[2]   Ruiz-Núñez B, Dijck-Brouwer DJ, Muskiet FA. The relation of saturated fatty acids with low-grade inflammation and

cardiovascular disease [J]. The Journal of Nutritional Biochemistry, 2016, 36: 1-20.

[3]  WHO, World Health Organization. Social Determinants of Health: Health Systems. 2014, Retrieved on November 13th. Accessed 10 march 2019.

[4]  Barbut S, Wood J, Marangoni A. Potential use of organogels to replace animal fat in comminuted meat products [J]. Meat Science, 2016, 122: 155-162.

[5]  Renzyaeva T. On the role of fats in baked flour goods [J]. Foods and Raw materials. 2013. 1(1): 19-25.

[6]  Mert B, Demirkesen I. Reducing saturated fat with oleogel/shortening blends in a baked product [J]. Food Chemistry 2016, 199: 809-816.

[7]  Galanakis CM, Tornberg E, Gekas V. Dietary fiber suspensions from olive mill wastewater as potential fat replacements in meatballs [J]. LWT-Food Science and Technology, 2010, 43(7): 1018-1025.

[8]  Lim J, Jeong S, Lee S. Evaluation of soybean oil-carnauba wax oleogels as an alternative to high saturated fat frying media for instant fried noodles [J]. LWT-Food Science and Technology, 2017, 84: 788-794

[9]  Herrero A, Carmona P, Pintado T, et al. Olive oil-in-water emulsions stabilized with caseinate: Elucidation of protein-lipid interactions by infrared spectroscopy [J]. Food hydrocolloids, 2011, 25(1). 12-18.

[10] Paneras E, Bloukas J. Vegetable Oils Replace Pork Backfat for Low-Fat Frankfurters [J]. Journal of Food Science, 1994, 59(4): 725-728

[11] Wassell P, Bonwick G, Smith CJ, et al. Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems-a review [J]. International Journal of food Science & Technololgy, 2010, 45(4): 642-655.

[12] Marangoni AG, Narine SS. Rheology fundamentals and structural theory of elasticity, Fat crystal networks [J]. CRC, 2004, 132-159.

[13] Davidovich-Pinhas M, Barbut S, Marangoni A. Development, characterization, and utilization of food-grade polymer oleogels [J]. Annual Review of food Science and Technology, 2016, 7: 65-91.

[14] De Vries A, Gomez YL, van der Linden E, et al. The effect of oil type on network formation by protein aggregates into oleogels [J]. RSC advances, 2017, 7(19): 11803-11812.

[15] Zhang M, Weiss R. Self-Assembled Networks and Molecular Gels Derived from Long-Chain, Naturally-Occurring Fatty Acids [J]. Journal of the Brazilian Chemical Society, 2016, 27(2): 239-255.

[16] Gravelle A, Davidovich-Pinhas M, Zetzl A, et al. Influence of solvent quality on the mechanical strength of ethylcellulose oleogels [J]. Carbohydrate Polymers, 2016, 135: 169-179.

[17] Co ED, Marangoni AG. Organogels: An alternative edible oil-structuring method [J]. Journal of the American Oil Chemists´ Society, 2012, 89(5): 749-780.

[18] Suzuki M, Hanabusa K. Polymer organogelators that make supramolecular organogels through physical cross-linking and self-assembly [J]. Chemical Society Reviews, 2010, 39(2): 455-463.

[19] Pernetti M, van Malssen KF, Flöter E, et al. Structuring of edible oils by alternatives to crystalline fat [J]. Current opinion in Colloid & Interface Science, 2007, 12(4-5): 221-231.

[20] Gao J, Wu S, Rogers M. Harnessing Hansen solubility parameters to predict organogel formation [J]. Journal of Materials Chemistry, 2012, 22(25): 12651-12658.

[21] Ma X, Sun X, Hargrove D, et al. A biocompatible and biodegradable protein hydrogel with green and red autofluorescence: preparation, characterization and in vivo biodegradation tracking and modeling [J]. Scientific reports, 2016, 6: 19370.

[22] Patel AR. Alternative routes to oil structuring (Vol. 820): Springer, 2015. 78p.

[23] Marangoni AG. Fat crystal networks: CR, 2004.

[24] Zhang J, Muirhead B, Dodd M, et al. An Injectable Hydrogel Prepared Using a PEG/Vitamin E Copolymer Facilitating Aqueous-Driven Gelation [J]. Biomacromolecules, 2016, 17(11): 3648-3658.

[25] Chen C, Terentjev E. Aging and metastability of monoglycerides in hydrophobic solutions [J]. Langmuir, 2009, 25(12): 6717-6724.

[26] Dassanayake LSK, Kodali DR, Ueno S, et al. Crystallization kinetics of organogels prepared by rice bran wax and vegetable oils [J]. Journal of oleo science, 2012, 61(1): 1-9.

[27] McClements DJ. Understanding and controlling the microstructure of complex foods: Elsevier, 2007.

[28] Rogers MA, Wright AJ, Marangoni AG. Crystalline stability of self-assembled fibrillar networks of 12-hydroxystearic acid in edible oils [J]. Food Research International, 2008a, 41(10): 1026-1034.

[29] Wright AJ, Marangoni AG. Time, temperature, and concentration dependence of ricinelaidic acid-canola oil organogelation [J]. Journal of the American Oil Chemist´ Society, 2007, 84(1): 3-9.

[30] Bot A, den Adel R, Roijers EC. Fibrils of γ-oryzanol+ β-sitosterol in edible oil organogels [J]. Journal of the American Oil Chemist´ Society, 2008, 85(12): 1127-1134.

[31] Weiss RG, Terech P. Molecular gels: materials with self-assembled fibrillar networks: Sprin Sci & B Media, 2006.

[32] Toro-Vazquez J, Morales-Rueda J, Dibildox-Alvarado E, et al. Thermal and textural properties of organogels developed by candelilla wax in safflower oil [J]. Journal of the American Oil Chemist´ Society, 2007, 84(11): 989-1000.

[33] Blake AI, Co ED, Marangoni AG. Structure and physical properties of plant wax crystal networks and their relationship to oil binding capacity [J]. Journal of the American Oil Chemist´ Society, 2014, 91(6): 885-903.

[34] Toro-Vazquez JF, Morales-Rueda J, Mallia VA, et al. Relationship between molecular structure and thermo-mechanical properties of candelilla wax and amides derived from (R)-12-hydroxystearic acid as gelators of safflower oil [J]. Food Biophysics, 2010, 5(3): 193-202.

[35] Zetzl AK, Marangoni AG, Barbut S. Mechanical properties of ethylcellulose oleogels and their potential for saturated fat reduction in frankfurters [J]. Food & function, 2012, 3(3): 327-337

[36] Sacco P, Furlani F, de Marzo G, et al. Concepts for developing physical gels of chitosan and of chitosan derivatives [J]. Gels, 2018, 4(67): 1-29.

[37] Martinez MJ, Pilosof AMR. On the relationship between pH-dependent β-lactoglobulin self-assembly and gelation dynamics [J]. International Food Research Journal, 2018, 25(2): 676-683

[38] Qiuyang X. PhD thesis. Understanding gelation systems with different gelling mechanisms in foods [J]. Rutgers University, New Brunswick, 2016, 121 p.

[39] Lu Y, Larock RC. Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications [J]. Chem Sus Chem, 2009, 2(2): 136-147.

[40] Davidovich-Pinhas M, Gravelle AJ, Barbut S, et al. Temperature effects on the gelation of ethylcellulose oleogels [J]. Food Hydrocolloids, 2015, 46:76-83.

[41] Martini S, Herrera M, Hartel R. Effect of cooling rate on crystallization behavior of milk fat fraction/sunflower oil blends [J]. Journal of the American Oil Chemist´ Society, 2002, 79(11): 1055-1062.

[42] Ye Y, Wagh A, Martini S. Using high intensity ultrasound as a tool to change the functional properties of interesterified soybean oil [J]. Journal of Agricultural and Food Chemistry, 2011, 59(19): 10712-10722.

[43] Zulkurnain M, Maleky F, Balasubramaniam V. High pressure processing effects on lipids thermophysical properties and crystallization kinetics [J]. Food Engineering Reviews, 2016, 8(4): 393-413.

[44] Herrera M, Hartel R. Effect of processing conditions on physical properties of a milk fat model system: microstructure [J]. Journal of the American Oil Chemist´ Society, 2000, 77(11): 1197-1205.

[45] Wang R, Liu XY, Xiong J, et al. Real-time observation of fiber network formation in molecular organogel: supersaturation-dependent microstructure and its related rheological property [J]. The Journal of Physical Chemistry B, 2006, 110(14): 7275-7280.

[46] Gravelle AJ, Barbut S, Quinton M, et al. Towards the development of a predictive model of the formulation-dependent mechanical behaviour of edible oil-based ethylcellulose oleogels [J]. Food Engineering, 2014, 143. 114-122.

[47] Xue P, Lu R, Yang X Et al. Self-assembly of Chiral Lipid Gelator Controlled by Solvent and Gelation Speed [J]. Chemistry: A European Journal, 2009, 15: 9824-9835.

[48] Bielejewski M, Łapinski A, Luboradzki R, et al. Solvent effect on 1, 2-O-(1-ethylpropylidene)-α-d-glucofuranose organogel properties [J]. Langmuir, 2009, 25(14): 8274-8279.

[49] Laredo T, Barbut S, Marangoni AG. Molecular interactions of polymer oleogelation [J]. Soft Matter, 2011, 7(6): 2734-2743.

[50] Cerqueira MA, Fasolin LH, Picone CSF, et al. Structural and mechanical properties of organogels: Role of oil and gelator molecular structure [J]. Food Research International, 2017, 96: 161-170.

[51] Batte HD, Wright AJ, Rush JW, et al. Phase Behavior, Stability, and Mesomorphism of Monostearin-oil-water Gels [J]. Food Biophysics, 2007, 2(1): 29-37.

[52] Toro-Vazquez JF, Morales-Rueda J, Torres-Martínez A, et al. Cooling Rate Effects on the Microstructure, Solid Content, and Rheological Properties of Organogels of Amides Derived from Stearic and (R)-12-Hydroxystearic Acid in Vegetable Oil [J]. Langmuir, 2013, 29(25): 7642-7654.

[53] Valoppi F, Calligaris S, Marangoni AG. Phase transition and polymorphic behavior of binary systems containing fatty alcohols and peanut oil [J]. Crystal Growth & Design, 2016, 16(8): 4209-4215.

[54] Pernetti M, van Malssen K, Kalnin D, et al. Structuring edible oil with lecithin and sorbitan tri-stearate [J]. Food Hydrocolloids, 2007, 21(5-6): 855-861.

[55] Rogers M. Spagnuolo PA, Wang T, et al. A potential bioactive hard-stock fat replacer comprised of a molecular gel Food [J]. Science Nutrition, 2017, 5(3): 579-587.

[56] Bot A, Agterof WG. Structuring of edible oils by mixtures of γ-oryzanol with β-sitosterol or related phytosterols [J]. Journal of the American Oil Chemist´ Society, 2006, 83(6): 513-521.

[57] Rogers MA, Wright AJ, Marangoni AG. Engineering the oil binding capacity and crystallinity of self-assembled fibrillar networks of 12-hydroxystearic acid in edible oils [J]. Soft Matter, 2008b, 4(7): 1483-1490.

[58] Rocha JCB, Lopes JD, Mascarenhas MCN, et al. Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil [J]. Food Research International, 2013, 50(1): 318-323.

[59] Blake A. The Microstructure and Physical Properties of Plant-Based Waxes and their Relationship to the Oil Binding Capacity of Wax Oleogels. 2015, http://hdl.handle.net/10214/8759. Accessed 20 March 2019

[60] Dassanayake LSK, Kodali DR, Ueno S, et al. Physical properties of rice bran wax in bulk and organogels [J]. Journal of the American Oil Chemist´ Society, 2009, 86(12): 1163

[61] Heijna MC, Theelen MJ, van Enckevort WJ, et al. Spherulitic growth of hen egg-white lysozyme crystals [J]. The Journal of Physical Chemistry B, 2007, 111(7): 1567-1573.

[62] Doan CD, Van de Walle D, Dewettinck K, et al. Evaluating the oil-gelling properties of natural waxes in rice bran oil: rheological, thermal, and microstructural study [J]. Journal of the American Oil Chemist´ Society, 2015, 92(6): 801-811.

[63] Martins AJ, Cerqueira MA, Fasolin LH, et al. Beeswax organogels: Influence of gelator concentration and oil type in the gelation process [J]. Food Research International, 2016, 84: 170-179.

[64] Jana S. Crystallization Behavior of Waxes. 2016.

https://digitalcommons.usu.edu/etd/5088. Accessed 22 march 2019.

[65] Du L, Brenner T, Xie J, et al. Gelation of Iota/Kappa Carrageenan Mixtures. In book: Gums and Stabilizers for the Food Industry 18: Hydrocolloid Functionality for Affordable and Sustainable Global Food Solutions, Editors: Peter A Williams, Glyn Phillips. 2017, 1-10.

[66] Mariz de Avelar MH, Efraim P. Alginate/pectin cold-set gelation as a potential sustainable method for jelly candy production [J]. LWT, 2020, 123: 109-119.

[67] Shirata Y, Wakasa A, Miura K, et al. Body heat responsive gelation of methylcellulose formulation containing betaine [J]. Food & Nutrition Science, 2017, 81(9): 1829-1836

[68] Joshi S, Lam YC, Tan BK, et al. Modeling of Thermal Gelation and Degelation of MC and HPMC Hydrogels [J]. ICBPE, 2006, 348654: 1-6.

[69] Mahnaj T, Ahmed SU, Plakogiannis FM. Characterization of ethyl cellulose polymer [J]. Pharmaceutical Development and Technology, 2013, 18(5): 982-989.

[70] Maity GC. Low molecular mass gelators of organic liquids [J]. Journal of Physical Sciences, 2007, 11: 156-171.

[71] Schaink H, Van Malssen K, Morgado-Alves S, et al. Crystal network for edible oil organogels: possibilities and limitations of the fatty acid and fatty alcohol systems [J]. Food Research International, 2007, 40(9): 1185-1193.

[72] Stortz TA, Zetzl AK, Barbut S, et al. Edible oleogels in food products to help maximize health benefits and improve nutritional profiles [J]. Lipid Technology, 2012, 24(7): 151-154.

[73] Kouzounis D, Lazaridou A, Katsanidis E. Partial replacement of animal fat by oleogels structured with monoglycerides and phytosterols in frankfurter sausages [J]. Meat Science, 2017, 130: 38-46.

[74] Sintang MDB, Danthine S, Patel AR, et al. Mixed surfactant systems of sucrose esters and lecithin as a synergistic approach for oil structuring [J]. Journal of Colloid and Interface Science, 2017, 504: 387-396.

[75] Swe MTH, Asavapichayont P. Effect of silicone oil on the microstructure, gelation and rheological properties of sorbitan monostearate-sesame oil oleogels [J]. Asian Journal of Pharmaceutical Sciences, 2018, 13(5): 485-497.

[76] Thaiudom S, Khantarat K. Stability and rheological properties of fat-reduced mayonnaises by using sodium octenyl succinate starch as fat replacer [J]. Procedia Food Science, 2011, 1: 315-321.

[77] Stortz TA, Marangoni AG. Heat resistant chocolate [J]. Trends in food science & technology, 2011, 22(5): 201-214.

[78] Zulim BDC, Marangoni AG, Smith A, Goff D. Development of Formulations and Processes to Incorporate Wax Oleogels in Ice Cream [J]. Journal of Food Science, 2013, 78(12): C1845-C1851

[79] Singh BB, Shakil NA, Kumar J, et al. Development of slow release formulations of β-carotene employing amphiphilic polymers and their release kinetics study in water and different pH conditions [J]. Journal of Food Science and Technology, 2015, 52(12): 8068-8076.