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Edible oleogels in molecular gastronomy

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Abstract

Experimental chefs and researchers have limited options when structuring lipid-based materials present in foods to include: liquids, solids, foams or emulsions. However, the application of gel technology for lipids is on the cusp of advancing into experimental culinary kitchens around the world. The possibility of utilizing edible oils (and even ethanol) to extract a hydrophobic flavor and then gel the material in a similar fashion as hydrocolloids gel water is now a reality. This review covers the three primary oleogels: ethyl cellulose, mixtures of γ -oryzanol and β -sitosterol and candelilla wax. © 2014 AZTI-Tecnalia. Production and hosting by Elsevier B.V. All rights reserved.

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Oleogels in foods

Modifying the physical state of foods has been a cornerstone of molecular gastronomy since its origins, and the ability to control and manipulate aqueous based systems has led to the creation of a gamut of materials including: solids, gels, liquids, and foams. When a component of a dish or food is primarily water, numerous strategies are well understood and in place to modify its physical state. It may be converted to a solid by simply cooling or evaporating a portion of the water, it can be modified to foam by whipping with air, CO₂

or N₂, or it can be gelled with one of the plethora of polymeric gelators. Polymeric hydrogelators allow complete control of the textural properties and in numerous cases allow the modification of the flavor release profile (Vilgis, 2012). Most typically, polymeric gelators, in aqueous solutions solidify as they are cooled and hence the state transition is an enthalpy-controlled reaction. This is the broadest group of gelators (i.e., gelation, agar-agar, starch, guar gum, locust bean gum, etc.) available to modernist chefs and is thoroughly reviewed by Martin Lersch (Lersch, 2010). The second strategy, also an enthalpy driven reaction, is to gel aqueous solutions by physically cross-linking the polymers using salts via the formation of salt-bridges (i.e., alginates and carrageenan) (Vega and Castells, 2012; Lee and Rogers, 2012; Campo et al., 2009). Finally, gels can also be driven to form via entropy driven state transitions whereby the gel forms at elevated temperatures and the reversible solution forms upon cooling (i.e., methyl cellulose) (Kato et al., 1978; de Moura et al., 2009). Unfortunately, these hydrocolloid based gelators are not soluble in hydrophobic liquids such as vegetable oils limiting their applications to aqueous systems.

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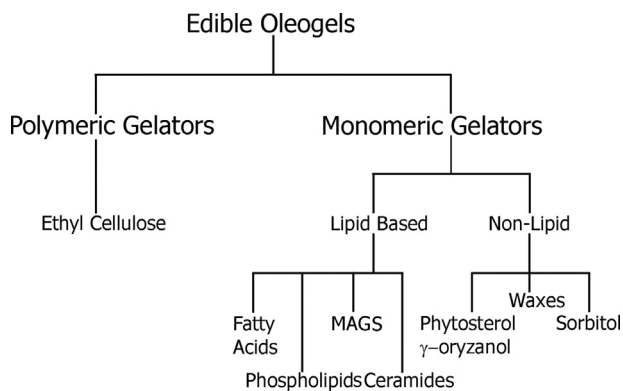


Fig. 1. Potential ingredient technologies to form oleogels.

Lipids are a major constituent of many dishes, because they provide desirable mouth-feel, flavor and impart solid-like properties to the food. Traditionally, processed foods, which contain high quantities of lipids also contain hard stock or modified hard stock fats consisting primarily of *trans* and saturated fats (Wassell and Young, 2007; Wassell et al., 2010). The macrostructure of fats and oils, including their viscoelastic properties, are highly influenced by both the nanoscale (triglyceride (TAG) composition and polymorphic form) and microstructural elements (fat crystal size and amount of solids) of the food (Awad et al., 2004; Tang and Marangoni, 2006c; Wesdorp et al., 2005). The elastic properties of lipids originate from the presence of long, straight-chain fatty acids. Upon cooling, the solubility of the hard stock TAGs decrease leading to a decrease in solubility causing phase separation and eventually nucleation followed by crystal growth. Since TAGs are large, anisometric molecules, numerous configurations in the solid states exist giving rise to three primary polymorphic forms: α , β' , and β . Depending on the desired material properties, mass and energy transfer can be modified selecting the desired form. The polymorphic arrangements stack TAGs into lamella within the crystals and it is these crystals that form a 3D network of clusters interacting via non-covalent interactions forming the final macroscopic network (Tang and Marangoni, 2006c, 2006a, 2006b). The major advantage of TAG structuring is the diversity of fatty acids and their possible molecular configurations, which allows for the physical properties to be tailored by changing the chemistry of the molecules or by modifying the processing conditions.

However, the ability to modify the structure of oils, in molecular gastronomy, is limited to changing the amount of solid hard stock fats, whipping in gas or generating emulsions. The ability to gel oil has yet to emerge as a viable technique in molecular gastronomy although numerous ingredient technologies exist (Fig. 1) (Rogers, 2009; Bot et al., 2009b; Perneti et al., 2007; Hughes et al., 2009). Herein we will report on three oleogels, ethyl cellulose, mixtures of β -sitosterol and γ -oryzanol and wax – specifically candelilla wax. Lipid based gelators, as well as sorbitol, structure oils in a very similar fashion to hard stock TAGs and as such will not be reviewed.

Polymeric gelators

Few polymeric oleogels exist due to the poor solubility of these compounds in edible oils. However, one extremely effective polymeric oleogelator has been identified – ethylcellulose (EC) (Laredo et al., 2011b; Marangoni, 2013). EC can create a solid elastic gel in oil (Co and Marangoni, 2012). EC is a linear polymer of 1,4- β -D-glucose units with ethoxy substitutions at carbons 2, 3, or 6 (Fig. 2A). It is synthesized from cellulose and when the degree of substitution reaches 2.3–2.6 (out of 3) the EC becomes soluble in organic oils. It has been found that an oleogel (Fig. 2B) can be formed when EC is heated in vegetable oil above its glass transition temperature at approximately 140 °C and subsequently cooled (Dey et al., 2011). The EC is able to partially solubilize in the oil, and once cooled, the EC polymers interact with each other and the oil, forming a gel network (Laredo et al., 2011a). These EC oleogels have been researched for their potential use in a variety of food products ranging from pure vegetable oils to heat-resistant chocolate (Stortz and Marangoni, 2013). This method has several shortcomings (Gravelle et al., 2012). A method was developed by Gravelle et al. (2012), which uses a convection oven with an overhead stirrer which offers the benefits of good temperature regulation leading to repeatable sample preparation times, minimal sample bubbling and the elimination of any granular particles. The requirement for EC to be heated above its glass transition temperature in the oil during gel manufacture leads to concerns about oil oxidation. Furthermore, any surfactants that are added to the system may be affected by the high heat and the EC is also known to start decomposing at temperatures above 170 °C (Gravelle et al., 2012). Therefore, the extent of oxidation and degradation of the system were studied during the manufacture of gels using the oven method.

It was found that the peroxide value (PV) and thiobarbituric acid, reactive substances in canola oil, increased over time while heated in the oven at temperatures above 140 °C (Gravelle et al., 2012). A holding time of 20 min was found to be the maximum heating time before the oil exceeded quality parameters for “fresh” oil (Codex Stan, 1981). Interestingly, it was found that gels made with a combination of fresh and rancid (PV > 10 meq/kg) canola oil displayed increasing mechanical strength (tested by back extrusion) with increasing proportions of rancid oil. This result was corroborated by measuring the mechanical strength of EC oleogels held for various amounts of time in the oven after reaching 140 °C. An unexpectedly large increase in mechanical strength was observed between 5–10 min holding time, which was attributed to dissolution of more of the EC rather than just an effect of increased PV. The increasing gel mechanical strength with increased PV can be attributed to the greater polarity of the oxidized oil that would increase the solubility of the EC in the oil leading to a stronger gel matrix.

Depending on the desired physical properties and the food material of interest vastly different gels may be required. Therefore, the properties of EC gels were studied using an array of formulation variables. EC is commercially available in

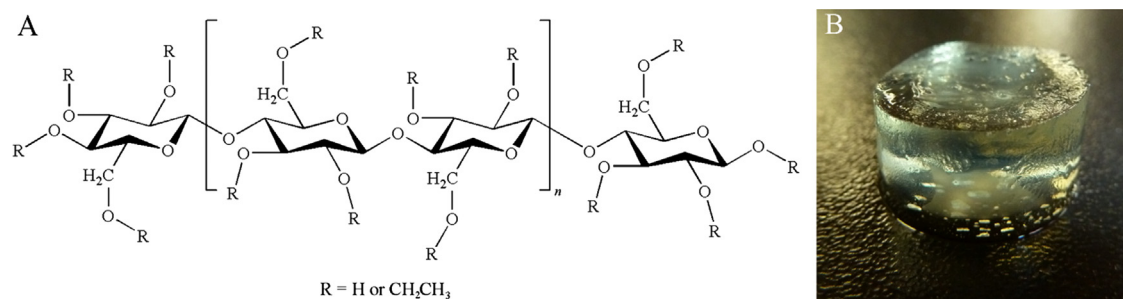


Fig. 2. (A) EC structure and (B) EC oleogel with 11% EC 20 cP in canola oil.

a variety of molecular weights that has been characterized by the manufacturer as the viscosity in centipoises (cP) of a 5% solution of EC in 80% toluene, 20% ethanol (EtOH). This work will focus on polymers with viscosities from 4–100 cP. These polymers all have a degree of substitution of approximately 2.5, which gives them the necessary solubility in the vegetable oils to form a gel. The gels structure as a function of EC concentration has been studied, using a variety of vegetable oils, as well as with the addition of edible surfactants such as glycerol mono-oleate (GMO). These surfactants can plasticize the EC and modulate the solubility of the EC in the oil (Dey et al., 2011).

The work of Laredo et al. (2011b) and Zetzl et al. (2012) showed that the mechanical properties of EC oleogels (hardness or elastic modulus) are affected by characteristics of the vegetable oil used. It was observed that the mechanical strength of the gels increased with increasing levels of unsaturation in the oil. A canola oil gel rich in oleic acid (18:1) was much softer than a flaxseed oil gel rich in linolenic acid (18:3). The differences observed were attributed to the packing of the fatty acids within the EC gel network. Denser oil, such as flaxseed, would pack more tightly in the EC network creating a stronger gel. Zetzl et al. (2012) went on to show that the EC gel hardness increases with increasing polymer molecular weight (MW) for all oils tested. This was expected, since the higher MW polymers are longer and would be able to form more network junction zones and polymer–oil interactions. The trend of increasing hardness with EC MW was not linear but closer to an exponential or power law function and was different depending on the oil used. Furthermore, the gel hardness increased with increases in EC concentration. EC gels contain a coral-like structure with many small pockets in which oil would be entrapped. The polymer network was quite thick, indicating the presence of bundles or groups of EC polymers making up the structure of the gel.

One key issue when developing a procedure to manufacture foods with EC gels is that these gels become solid like at very high temperatures and when sheared after setting the gel irreversibly breaks. Breaking the gel can cause loss of its functionality leading to loss of hardness and oil leakage among other things. Fortunately, this issue has been addressed by the development of EC oleogels with thixotropic properties. Thixotropy is used to describe a material that exhibits both shear thinning and an increase in viscosity upon removal of the

shear (Daubert and Foegeding, 2010). A thixotropic EC gel could be incorporated into a food product, sheared at various stages during manufacture, and overtime the gel would regain its mechanical properties and functionality. Incorporation of glycerol mono-oleate (GMO), a common food-grade surfactant that has been used previously when preparing EC gels to plasticize the polymer, can generate a thixotropic gel. At this ratio of GMO:oil gels made with 5–8% EC of various molecular weights (viscosities 10–45 cP), a large variety of vegetable oils showed shear thinning behavior and full viscosity recovery upon removal of the shear after storage for one week. These gels show great potential for use in food products, which require shear during manufacture.

The above research has provided much valuable knowledge that can be used to manufacture EC oleogels for a variety of food applications. Zetzl et al. (2012) studied the use of EC oleogels to replace a portion of the beef fat in a finely comminuted frankfurter. It was found that frankfurters made with ungelled canola oil were much harder and chewier than those made with beef fat. However, when the canola oil was added as an EC oleogel, both the hardness and chewiness of the frankfurter were not significantly different from the beef fat control. The differences in textures can be attributed to differences in the fat globule size (Fig. 3) in the batter. During manufacture of finely comminuted meat products, the proteins become solubilized allowing them to coat the fat globule interface and form a continuous protein network. A large surface area of fat would lead to more protein adhesion resulting in a harder product (Youssef and Barbut, 2009). As displayed in Fig. 2, the batter made with beef fat showed the largest globule size, while the oleogel had smaller fat globules and the canola oil had miniscule globules. Gelling the oil allowed it to behave more similarly to the beef fat, resisting chopping and preventing distribution and emulsification into tiny oil droplets. Although the beef fat and oleogel samples did not show the same fat globule size distribution, it was concluded that the texture of the frankfurter is largely affected by the presence of fat globules 9–24 μm in size. Within this range that fat globule size distribution for the oleogel and beef fat nearly match, the canola oil control contains globules mostly smaller than 9 μm. Therefore, the large proportion of very small oil globules in the canola oil sample contributed to its harder and chewier texture compared to the gel and beef fat products. This shows that gelling a vegetable oil is a viable way to achieve a more nutritious fatty acid profile

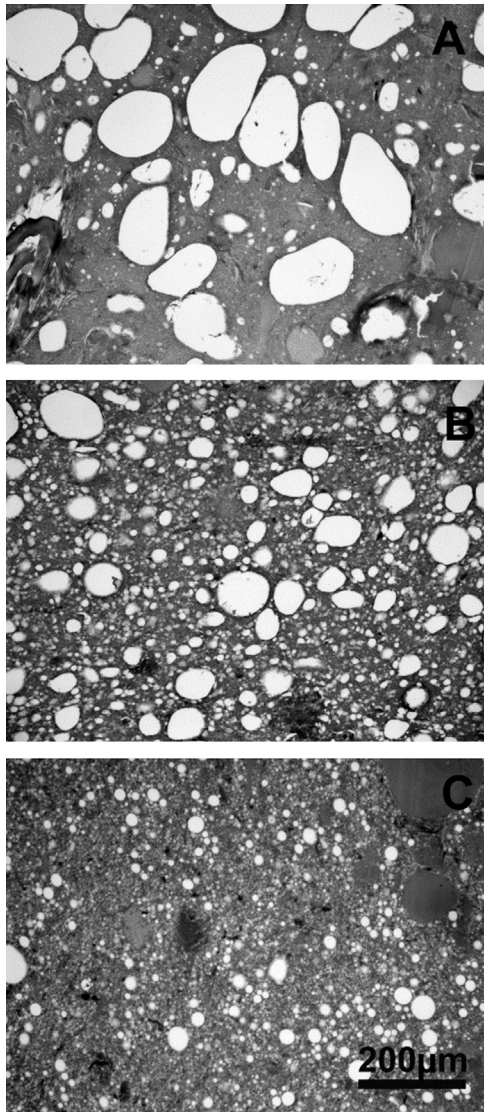


Fig. 3. Cooked frankfurter batter micrographs with (A) beef fat, (B) EC oleogel, and (C) oil. White circular globules represent fat globules and the darker surrounding area is the protein network.

in a food product without compromising the textural quality of that product.

A second application explored for the use of EC in chocolate to allow it to hold its shape or resist melting up to temperatures of 40 °C. Previous research in this area has utilized techniques including: increasing the melting point of the fat phase, enhancing the network microstructure, and addition of an oil binding polymer. Details of these techniques have been summarized in the review by [Stortz and Marangoni \(2011\)](#). A solution of 20% EC in 100% ethanol (EtOH) was prepared and then added at levels around 10% to a molten, conventional chocolate. The EC was mixed with the chocolate then molded, cooled, and demolded. The resulting chocolate was then placed in an incubator to evaporate the EtOH. The EtOH-free chocolate was tested for heat resistance by performing a compression test using a texture analyzer with the sample at 40 °C to measure the hardness ([Fig. 4](#)). Clearly the sample

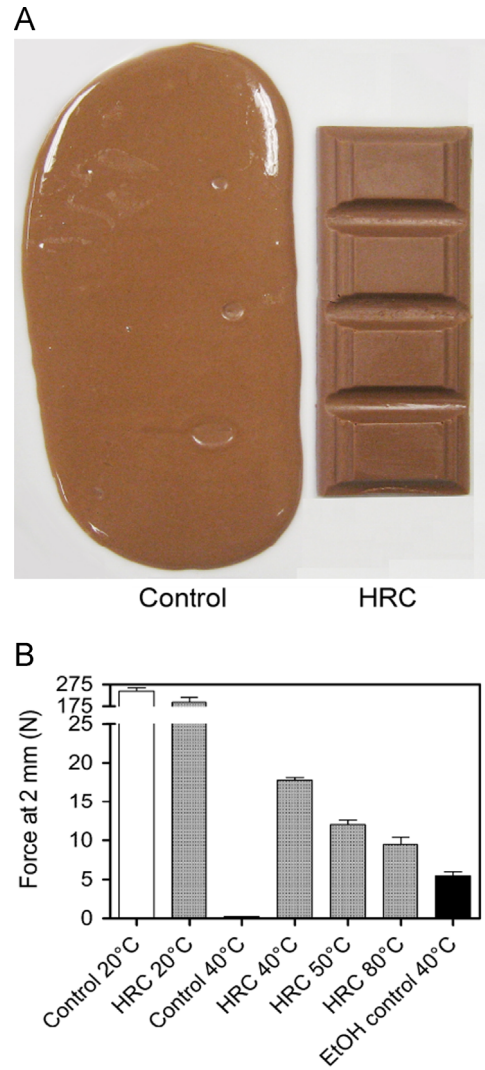


Fig. 4. (A) Control and HRC after 2 h in an incubator at 40 °C; (B) hardness of controls and HRC at various temperatures measured using a texture analyzer.

that contained EC showed great heat resistance even at extremely high temperatures while the control chocolate was completely melted. Interestingly, a control chocolate that was made with added EtOH showed some heat resistance but not nearly as much as the EC-containing sample. The heat resistance was found to depend on the type of chocolate used; milk and white chocolates were harder than dark chocolates, and this was thought to be primarily a result of greater sugar concentrations in milk and white chocolates. These changes will dramatically alter the sensory attributes of chocolate and may provide a new culinary experience. Furthermore, it was found that the heat resistance was dependent on the EC concentration, or the EC:EtOH ratio, in the initial solution. Contrary to previous results, which have shown large differences between EC of different molecular weight, altering the EC molecular weight had no significant effect on heat resistance. This research demonstrates that EC can be used not only for its ability to gel oil and improve fatty acid profiles of food products but also to impart added functionality.

There are likely many more food applications where EC oleogels will be useful. Some areas which show promise include: improving the oil binding in peanut butter, replacing a portion of the shortening used in laminated pastries to alter fatty acid profile, reduce oil migration from the cream filling of a sandwich cookie to prevent softening of the cookie, and reduce oil migration from a chocolate coated cookie to reduce problems with blooming. Further research will reveal the vast potential of EC as a valuable food ingredient.

Molecular oleogels

The second major strategy to gel oil is to use monomeric gelators, which assemble via non-covalent interaction to form fiber-like crystallites that then interact to form 3D networks. This strategy is based on crystals that do not grow unrestrictedly in three dimensions as is traditionally the case. In this section, an example of the latter will be introduced. The creation of molecular gels, capable of self assembling into fibers and creating a complex supramolecular network, requires an intricate understanding of the molecular scale interactions. The ability of certain molecules to nucleate and to self-assemble into fibers in edible oils requires a careful balance among opposing parameters including solubility and those that control epitaxial growth into axially symmetric elongated aggregates. In recent years, molecular gels, comprised of low molecular-mass organic gelators (LMOGs), have experienced a surge in interest due to their potential applications and fundamental importance (Terech and Weiss, 1997; Abdallah and Weiss, 2000; Weiss and Terech, 2006). Molecular gels often form a 3D continuous network embedded in a low polarity liquid driven, by specific intermolecular interactions to build the primary structures of the fibrillar aggregates (Terech et al., 1994). Typically, these physical interactions include H-bonding, electrostatic forces, π - π stacking, and London dispersion forces (Mallia et al., 2009). The ability for these molecules to self-assemble into rod-like structures requires a careful balance among opposing parameters including solubility and those that control epitaxial growth into elongated aggregates (Suzuki et al., 2003). On a molecular level, the required characteristics are not well understood. Two molecular gelators, which have tremendous potential for use in molecular gastronomy include mixtures of phytosterols and γ -oryzanol (Wassell et al., 2010; Rogers, 2009; Bot et al., 2009b; Bot and Agterof, 2006; Duffy et al., 2009; Rogers et al., 2010) and candelilla wax (Pérez-Martínez et al., 2007; Toro-Vazquez et al., 2010).

Amongst other features, oil-structuring alternatives to TAGs should comprise a number of different aspects. First and foremost, the structurant should be food grade. This is probably the most difficult aspect, as it involves not only safety and history of human consumption of the ingredient, but also many local legal aspects. It should therefore not be taken for granted that the examples shown in this paper can be applied in food applications without careful study of the local legislation. Since the admission of an ingredient or a new application thereof may require so much effort, it is imperative

therefore that the alternative structurant brings something unique too – something that cannot be delivered through traditional oil structuring with triglycerides. One of these unique features of edible oleogels is their ability to reduce saturated fatty acid content (or even the trans fatty acid content in parts of the world where this has not been removed yet) in the structured oil. This is a rather intellectual rationale from a consumer point of view, however. It would be much better if there were a reason to desire such alternatives that is much more directly appealing on an emotional level. One potential candidate for such an attractive feature is the transparency of some oleogels. This is caused by the small size of the building blocks compared to the wavelength of visible light, which sets them apart from regular triglyceride-structured oils. The β -sitosterol and γ -oryzanol oleogel is an example of such a system.

Plant sterols and sterolesters are components that are found naturally at low levels in vegetable oils. β -Sitosterol can be found in a wide range of vegetable oils, whereas γ -oryzanol is a component from rice bran oil. In an esterified form, β -sitosterol is also known as the active ingredient in a number of blood-cholesterol lowering foods. These molecules are composed of an androsterol group with an attached alkyl chain on one side, and in the case of γ -oryzanol a ferulic acid moiety on the other side. It has been shown that molecules of β -sitosterol and γ -oryzanol can stack, mainly aligning their androsterol groups (Pernetti et al., 2007; Laredo et al., 2011a). Infrared spectroscopy reveals a weak band around 3441 cm^{-1} , indicative of intermolecular hydrogen bond formation (Rogers et al., 2010; den Adel et al., 2010). The hydrogen bond prevents perfectly parallel stacking of both molecules, and forces a slightly wedged conformation in the molecular assembly. As a direct consequence, these mixed molecules cannot form a regular three-dimensional crystal when stacked aligned on top of each other. Instead, a curved assembly is formed. Small-angle x-ray scattering (SAXS) reveals that the curved linear crystal takes the shape of a helical ribbon over longer length scales (Bot et al., 2009b, 2008), which, in essence, is a hollow tubule dispersed in and filled with the oil phase. This microstructure is part of complex phase behavior of mixtures of the two components in edible oil (AlHassawi and Rogers, 2013).

The pronounced features in the SAXS data (in particular the sharp minima in the scattering curves) indicate that the structure is very monodisperse and well-defined. In fact, sterol+sterolester concentration or ratio of both components, and to a lesser extent even sterol type, oil type or temperatures hardly affect the scattering pattern. Only the use of a quite polar organic oil, like eugenol, changes the scattering pattern somewhat (Sawalha et al., 2012). Some of the insensitivity of the SAXS scattering patterns to the abovementioned variations is explained by the small differences in scattering properties between structurant and organic oil. These differences can be enhanced by employing small-angle neutron scattering (SANS) in combination with deuterated organic oils. Deuterated TAGs are not readily available, and therefore SANS experiments have been executed on oleogels based on mixtures

of edible oils with deuterated decane (Bot et al., 2012). These experiments revealed more details on the tubule structure. The tubule appears to consist of a double walled structure, in which the outward-pointing ferulic acid groups of the γ -oryzanol (which are grafted at roughly half the density compared to the androsterol groups that occur in both β -sitosterol and γ -oryzanol), can be identified separately from the stacked androsterol groups. The overall diameter of the tubules is ~ 10 nm and the wall thickness is ~ 2 nm (Bot et al., 2012). It might be possible to refine this model by additional experiments with even more careful contrast variation between structurant and oil.

These approximate dimensions are confirmed in two types of microscopic studies, Atomic Force Microscopy (AFM) (Bot and Flöter, 2011) and Transmission Electron Microscopy (SEM) (Sawalha et al., 2012). Both techniques indicate the presence of fibrils with a width of ~ 10 nm in the sample and an extreme aspect ratio (Fig. 5). The images suggest a tubule length of the order of micrometers. The images also indicate that the tubules have a tendency to aggregate laterally. Aggregation as such is a prerequisite for gelling, though this should preferably involve cross-linking, rather than alignment of the tubules, as large-scale parallel aggregation of the tubules would reduce the effectiveness of the structurant – and on top of that interfere with the possibility to obtain a transparent oleogel. A minimal amount of 2–4% structurant on oil phase is needed to create a gel, though firmer gels are obtained at higher concentrations. The optimal mixture is a 1:1 molar ratio of β -sitosterol and γ -oryzanol, i.e. a $\sim 40:60$ ratio on weight basis. The process to form a gel is very simple: the structurant is dissolved in the oil, which typically requires ~ 140 °C. Subsequently the dissolved structurant and oil mixture is cooled down and the oleogel forms. It should be noted, however, that gelling may be delayed due to the occurrence of a metastable supercooled state, especially in systems that are rich in γ -oryzanol and at relatively low structurant concentrations – say below 10% (Bot and Agterof, 2006; Bot et al., 2008). In such cases, it may be desirable to cool the samples in the fridge, though for most conditions, the samples can be cooled simply under ambient conditions. The gelling process is reversible and can be repeated by applying a new heating and cooling cycle. The resulting transparent gels have the color of the oil phase that was used to produce the gel. The gels are quite firm and are much firmer under compression than under

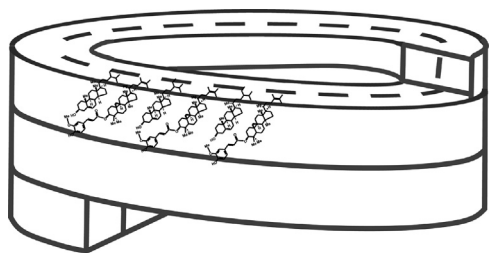


Fig. 5. Schematic representation of a double-walled helical structure due to wedged stacking of β -sitosterol and γ -oryzanol molecules, with the ferulic acid moieties of the γ -oryzanol pointing outwards. The resulting tubule has a diameter of ~ 10 nm.



Fig. 6. Shaped transparent 10% (40% β -sitosterol + 60% γ -oryzanol) oleogels in sunflower oil. No special processing was required: dissolved β -sitosterol and γ -oryzanol in sunflower oil was poured in a standard silicone chocolate mold that was cooled in a fridge.

shear (Bot and Agterof, 2006). As a result, the gels are somewhat slippery when handled. One of the attractive aspects is that the firmness of the oleogels allows them to be shaped in various forms, and the gels keep their shape (Fig. 6). This sets these systems apart from TAGs-structured oleogels, as these would be opaque.

If gelling is done under controlled conditions, e.g. in a rheometer, it is found that small-amplitude oscillations may increase the reproducibility of the gelling rate (Bot and Agterof, 2006). In particular, this has been demonstrated for conditions that are sensitive to supercooling, and the oscillations apparently disturb the metastable state. However, the amplitude of the mechanical disturbance cannot be too high. This reflects a delicate balance between inducing local flow to increase growth of and interaction between the tubules due to modest flow on the one hand, and the attrition of aggregates due to intense flow on the other hand. The melting behavior of these oleogels can be studied by means of differential scanning calorimetry (DSC) (Sawalha et al., 2012, 2011) or small-deformation rheology (Bot and Agterof, 2006). The mixture of two pure components has a well-described melting point around ~ 120 °C, but the dissolution temperature is lower when diluted in oil – the dissolution temperature decreases with decreasing concentration of the structurant mixture (Bot and Agterof, 2006; Sawalha et al., 2011, 2013). In theory, the dissolution temperature can be reduced to mouth temperature by reducing the structurant concentration. In practice, however, the firmness of the oleogel also reduces with reducing structurant concentration. Unfortunately, the particular properties of the β -sitosterol + γ -oryzanol mixture do not provide sufficient firmness under conditions of use to introduce it as a straightforward replacement of crystallizing fats.

Another limitation of the β -sitosterol + γ -oryzanol structuring system is its sensitivity to the presence of water. Since the self-assembly is based on the formation of intermolecular hydrogen bonds between β -sitosterol and γ -oryzanol, it can be understood that the introduction of water will interfere with tubule formation. Indeed, infrared spectroscopy has shown that intramolecular hydrogen bonding does not persist in emulsions in which the samples have had sufficient time to equilibrate

(den Adel et al., 2010). Light microscopy shows that long fibrillar crystals form during prolonged storage, which are characteristic for β -sitosterol monohydrate crystals (Bot and Flöter, 2011). The consistency of the emulsion decreases during storage. The rate of the monohydrate formation process in emulsions can be decreased in two ways (Sawalha et al., 2012): the type of oil phase can be changed to reduce the water solubility in the oil and will limit transport of water from the aqueous phase to the structurant tubules; and a reduction of water activity of the water phase will reduce the affinity β -sitosterol to water relative to the water phase. The first approach will not have sufficient impact within the realm of normal edible oils to achieve stability during storage. The latter is feasible if the amount of water phase in the full formulation is sufficiently low to allow the high levels of salt or sugar in the water phase without contributing excessive amounts in the final product.

Overall, the β -sitosterol and γ -oryzanol system in edible oil is one of the more systematically investigated systems in the field of oleogelation. In particular, some excursions have been made to test related mixtures – like alternative sterols (Bot and Agterof, 2006; Bot et al., 2009a), and alternative oils (Sawalha et al., 2012). The main gap in current knowledge is in the area of alternative sterolesters. Little is known about introducing alternatives to the ferulic acid group. A straightforward replacement by (edible oil) fatty acids does not lead to oleogelation (Bot et al., 2009a), probably as a result of the high solubility of the obtained sterol-ester. A better understanding on the role of the acid group in the sterol-ester would be desirable, explaining whether the ferulic acid can be replaced by alternatives and whether these alternatives could lead to reduced sensitivity for the presence of water. This will involve synthesis of sterolesters, because there is only a limited range of commercially available sterolesters, possibly in combination with molecular modeling techniques as a first screening.

Candelilla wax oleogels

Candelilla wax (CW) is approved by the FDA (under regulations 21CFR, 175.105, 175.320, 176.180) as a food additive, obtained from the leaves of a small shrub (*Euphorbia cerifera* and *Euphorbia antisiphilitica*) native to northern Mexico and the southwestern United States. CW typically is used as a glazing agent, binder for chewing gums and as a substitute for carnauba wax and beeswax in different food systems. Reports on the CW composition indicate high proportions of *n*-alkanes with 28–33 carbons (≈ 44 –45%), esters of aliphatic acids and alcohols (≈ 6 –7.4%), aliphatic acids with 18–34 carbons (≈ 15 –18.8%), aliphatic alcohols with 24–34 carbons (≈ 5 –7.6%), alcohols of penta-cyclic triterpenoids (21–23%) and esters of alcohols of penta-cyclic triterpenoids (1.9–2.2%). Of the *n*-alkanes present hentriacontane is the major constituent ($C_{31}H_{64}$; $75.9\% \pm 0.1\%$) with lower concentrations of nonacosane ($4.2\% \pm 0.1\%$; $C_{29}H_{60}$), triacontane ($4.2\% \pm 2.0\%$; $C_{30}H_{62}$), dotriacontane ($2.8\% \pm 0.4\%$; $C_{32}H_{66}$), and tritriacontane ($9.9\% \pm 0.4\%$; $C_{33}H_{68}$)

(Alvarez-Mitre et al., 2013). Numerous authors have investigated CW as potential food grade oleogels (Alvarez-Mitre et al., 2013; Alvarez-Mitre et al., 2011; Bósquez-Molina et al., 2003; Chopin-Doroteo et al., 2011; Dassanayake et al., 2009; Hagenmaier and Baker, 1996; Morales-Rueda et al., 2009a, 2009b; Saucedo-Pompa et al., 2007; Toro-Vazquez et al., 2007, 2009, 2013). Although the phase behavior and functional properties of CW in foods has been primarily associated with the assembly of *n*-alkanes, other components such as pentacyclic triterpenoids also effect gelation (Alvarez-Mitre et al., 2013).

Oleogelation is easily achieved by heating the gelator in an oil (i.e., vegetable oils) until it becomes soluble, and then cooling the solution. CW is not an exception to this behavior. Solution-gel transition temperatures (T_{Cr}) have been probed for CW, in safflower oil, at various concentrations (0.5% to 6%) using two cooling rates (1 and 10 °C/min) by DSC, rheology, and textural measurements (Morales-Rueda et al., 2009a, 2009b; Toro-Vazquez et al., 2007). The results of these investigations illustrate that well-structured, opaque gels are obtained at CW concentrations $\geq 2\%$ (Fig. 7) even when the gelation temperature is 25 °C. However, at CW concentrations $< 2\%$ CW a gelation temperature ≤ 5 °C is required to achieve an elastic gel (Toro-Vazquez et al., 2007). The minimum CW concentration required to develop a 3D network capable of physically entrapping vegetable oil is temperature dependent. Additionally, those studies showed that T_{Cr} and T_M (i.e., the melting temperature) have a logarithmic dependence on CW concentration. In contrast, the enthalpy, or energy released during gelation (ΔH_{Cr}) and melting (ΔH_M) showed a linear direct relationship with CW concentration. These thermal parameters are independence of the number of thermal cycles (i.e., heat and cool cycles) (Toro-Vazquez et al., 2007), pointing out the thermo-reversible behavior of CW oleogels.

Cooling rate have also been shown to effect the thermal behavior of CW oleogels with implications on the rheological

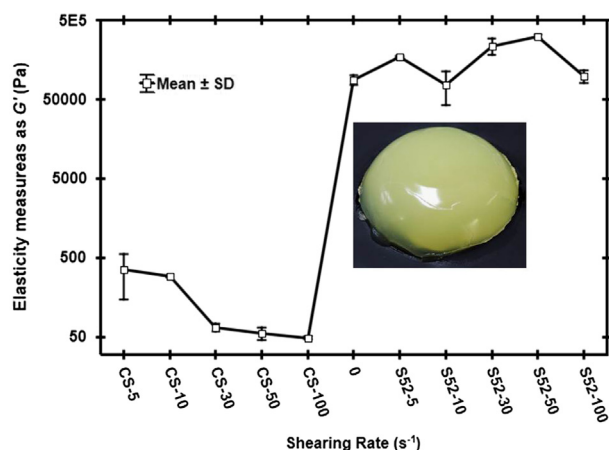


Fig. 7. Elastic modulus of 3% CW gels in safflower oil, obtained statically (0 s^{-1}), under continuous shearing (CS) from melt to the end of self-assembly at 5 s^{-1} (CS-5), 10 s^{-1} (CS-10), 30 s^{-1} (CS-30), 50 s^{-1} (CS-50) and 100 s^{-1} (CS-100) and shearing (S) at 5 s^{-1} (S52-5), 10 s^{-1} (S52-10), 30 s^{-1} (S52-30), 50 s^{-1} (S52-50) and 100 s^{-1} (S52-100) until 52 °C is reach and then quiescently cooling under static conditions (S).

and textural properties of the (Morales-Rueda et al., 2009a, 2009b; Toro-Vazquez et al., 2007). Shear rate and duration of shearing the CW-vegetable oil solution, have a profound effects on the viscoelastic properties of CW oleogels (Alvarez-Mitre et al., 2013, 2011; Toro-Vazquez et al., 2013). Within this framework, solutions of CW in vegetable oil cooled at 1 °C/min results in oleogels with higher T_{Cr} and ΔH_{Cr} than those oleogels developed at 10 °C/min. This behavior is explained considering that during cooling, the thermodynamic driving force for gel formation changes faster as cooling rate increased. Consequently, at high cooling rate (i.e., 10 °C/min) gelator molecules, such as the hentriacontane and other *n*-alkanes present in CW, have less time to organize in a solid phase than at 1 °C/min. As a result, oleogels developed at higher cooling rates require lower temperature (i.e., lower T_{Cr}) to achieve the molecular packing for crystal formation, have lower level of molecular organization in their assembly units (i.e., lower ΔH_{Cr}), and achieve smaller aggregate size. This results in CW oleogels developed at 1 °C/min having higher elasticity than oleogels developed at 10 °C/min. In spite of this, the solid content present in oleogels obtained at 1 °C/min was similar or lower than the crystal mass present in the oleogels developed at 10 °C/min (Morales-Rueda et al., 2009a, 2009b; Toro-Vazquez et al., 2007).

Chopin-Doroteo et al. (2011) showed that the application of continuous shearing (i.e., 600 s⁻¹) during oleogelation of 3% CW in safflower oil results in the formation of weaker gels than the oleogels developed quiescently. It appears that the application of shear at temperatures below T_{Cr} , does not allow the establishment of permanent junctions among the aggregates (Wang et al., 2006). 3% CW solutions were also gelled under static conditions by either applying a particular shear rate (30 to 600 s⁻¹) constantly during cooling (CS) or just during cooling from 90 °C to 52 °C then continuing the cooling under static conditions (S52) (Alvarez-Mitre et al., 2013). Gels formed statically, compared to those gelled under constant shear (CS) resulted in oleogels that were poorly structured with a decreased elasticity (i.e., lower elastic modulus, G') and aggregate size as shear rate increased (Chopin-Doroteo et al., 2011). In contrast, all shear rates investigated with shear applied until 52 °C (CS52) formed oleogels with larger aggregates, higher elasticity and resistance to deformation than the oleogels developed statically or with CS (Fig. 7). The microstructural and rheological analysis suggested that flow produced by S52 conditions induced molecular alignment of CW aggregates at temperatures above the onset for CW assembly. This would result in the development of mesophase precursors that upon further cooling under static conditions crystallize and develop a 3D network with more crystal-crystal interactions and thus higher elasticity. It is concluded that shearing and the duration of application, determined aggregate size and the supramolecular interaction throughout the 3D network.

Conclusion

There are numerous new technologies with regards to structuring oils that are on the verge of appearing in

experimental kitchens around the world including ethyl cellulose, combinations of β -sitosterol and γ -oryzanol and waxes. These three technologies, with diverse potentials, may be used to vary the structure in everything ranging from liquid oils, to chocolate to comminuted meat products. In a similar fashion to hydrocolloids, these different gels vary in appearance from opaque to transparent gels, in hardness from soft to hard gels and in melting profile from thermally stable to unstable gels. Solid vegetable or fish oils can now be created and tailored without uses other sources of traditional fats such as lard or butter imparting new and exciting sensory experiences yet to be experienced by the consumer!

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