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Novel trans fat replacement strategies Fan C Wang, Andrew J Gravelle, Alexia I Blake and Alejandro G Marangoni



The requirement for removing partially hydrogenated oils (PHOs) in food products by the U.S. Food and Drug Administration (FDA) is challenging the food industry to seek out healthy replacements that do not change the physical and sensory properties of end products. This article reviews novel strategies to structure liquid oils as PHO alternatives. The oil structuring mechanisms of ethylcellulose oleogels, plant-based wax oleogels, and monoglyceride-structured emulsions are discussed in detail. The structural and mechanical properties of such systems can be tailored to mimic that of PHO based fat systems. These oil-structuring methods show promise for applications in PHO-free products.

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Background

The US FDA recently announced its decision to finalize the removal of the GRAS (generally recognized as safe) status from partially hydrogenated oils (PHOs), and have provided a three-year mandatory compliance period, ending June 18, 2018. This decision was made in an attempt to eliminate industrially-produced *trans*-fats from the food supply, as PHOs presently represent the most significant dietary source of artificial *trans*-fatty acids. In the wake of this decision, companies are now faced with the challenge of finding viable replacements for PHOs which minimize the impact on organoleptic properties and consumer acceptance. This will be particularly difficult in certain systems which depend on the unique functional properties of such fats, such as the plasticity of laminating shortenings used in puff pastries and the specific melting profiles of confectionary fats.

Hard-stock fats such as PHOs contribute to the desirable structural, functional, and sensorial properties of food matrices. Consequently, they cannot generally be directly replaced with liquid oils without negatively impacting the organoleptic properties of the end product. A first order approach to the problem of replacing *trans*-fats is to substitute them with fats high in saturated fatty acids, such as palm fat, fully hydrogenated vegetable oils and animal fat [1–3°]. However, though the influence of dietary saturated fats on health has recently taken a more positive light, consumer perception remains generally negative [4–7]. Therefore, the use of such fats to replace PHOs should not be considered a viable industry-wide alternative to remove artificial *trans*-fats.

In recent years, the non-triglyceride structuring of edible oils (i.e. oleogelation) has shown strong potential as a means to replace hard-stock fats in food products. A variety of different systems have been identified which can impart solid-like properties on edible oil. These can be categorized into four main strategies: (i) the formation of a three-dimensional network of crystalline particles; (ii) self-assembled fibrillar networks of low molecular weight oleogelators, (iii) polymer gelators, and (iv) structured emulsions [3[•],8–11[•]]. Some of the oleogelators thus far identified may be subject to regulatory restrictions as direct food additives, while others may be limited in their versatility. This review will briefly outline a few of the more promising, functionally diverse oleogel systems, which have recently been intensively investigated for food applications [9–13]. These include the hydrophobic polymer ethylcellulose, several plant-based waxes, and monoglyceride-based structured emulsions.

Polymer oleogelators

In recent years, structuring liquid oils through the use of polymers has shown much promise for food applications. Presently, two main strategies have been identified: (i) directly dispersing a hydrophobic polymer in the oil phase and (ii) indirect, facile methodologies which involve templating hydrophilic/amphiphilic polymers. In the past few years, the latter strategy has been exploited by Patel *et al.*, who have successfully identified and characterized several polymer-based oleogel systems using both foam [14] and emulsion [15–17] templating methodologies. The main drawback of these systems is that they require the use of energy intensive processes, both to produce the initial foam/emulsion, and the subsequent dehydration step necessary to produce the templated structure. These critical templating steps may therefore limit industry

acceptance. Additionally, these systems are inherently limited in their capacity to mimic the textural properties of hard-stock fats, as they must be sheared as a final step to produce a semi-solid gel-like structure that exhibit little plasticity. Currently, the only known polymer that can be directly dispersed in edible oils for gelation is ethylcellulose (EC). EC is a semi-crystalline derivative of cellulose which is commercially produced to have an ethoxyl substitution of ~ 2.4 [18]. EC is soluble in a variety of organic solvents, and exhibits a glass transition temperature (T_a) at ~130 °C [19], above which EC can be dispersed in edible oils. Subsequently cooling the mix induces the formation of inter-polymer hydrogen bonds, creating a three-dimensional entangled polymer network in which the liquid oil is entrapped (Figure 1) [12,20,21]. Some examples of applications which have been evaluated include reduction of saturated fats in frankfurter-style meat products [12] and eliminating oil migration in model cream fillings.

As EC oleogels must be heated in excess of $130 \,^{\circ}$ C to induce gelation, the influence of temperature on the integrity of the oil phase is of obvious concern and antioxidants may be added to reduce oil oxidation. This issue was addressed by Gravelle *et al.*, and a controlled heating method was proposed, so as to minimize the effects of the heat treatment on the oil phase [22]. The versatility of EC oleogels can be attributed to the array of

Figure 1



Top: Schematic diagram describing the factors which can be used to modify the mechanical and textural properties of EC oleogels. *Bottom*: Self-supporting EC oleogel (left) and SEM image of the internal polymer network (right).

Additional means of modifying gel strength have also been identified, such as thermal annealing, altering solvent polarity, and addition of surface active small molecules. Reheating set EC oleogels to 80–100 °C for one hour (i.e. below T_g) has been shown to significantly increase their mechanical strength. This was attributed to a partial rearrangement of the hydrogen-bonding network supporting the gel that leads to a more extensive/ efficient gel network [24^{••}].

Polarity of the oil phase strongly impacts both the mechanical and textural traits of EC oleogels [25]. It was recently shown that addition of castor oil to the oil phase increases the solvent polarity, and produced up to an ~8-fold increase in gel strength (Figure 2a) [26^{••}]. Conversely, mineral oil (a non-polar solvent) deteriorated the ability of EC to form a gel. The influence of these oils on gel strength was interpreted using Hansen solubility theory [27]. This formalism was developed to interpret solvent-polymer compatibility using the dispersive, polar, and hydrogen bonding interaction energies. According to this theory, optimal dissolution can be achieved by minimizing the interaction distance between the polymer and solvent, $R_{\rho s}$ (see Figure 3c) [27]. However, consistent with recent studies investigating 12-hydroxystearic acid organogels [28] and EC gels of glycerol monooleate/vegetable oil blends [29[•]], EC/oil interactions could be optimized by minimizing the difference in the hydrogen bonding parameters alone, as confirmed by the zero shear rate viscosity (Figure 3d) [26^{••}]. Finally, polar, surfactant-like small molecules such as oleic acid and oleyl alcohol have a dramatic influence on gel strength, particularly at low incorporation levels (as low as 0.25 wt%) [26**]. The influence of these additives on the relative increase in gel strength was shown to fit a characteristic site-specific binding curve, up to a supplementation level of ~7.5 wt%, according to the equation $F_{rel} = 1 + F_{rel}^{\max}$. $[\phi_s/(K_d + \phi_s)]$ (see Figure 2b). Further addition led to an excess of these molecules that had a plasticizing effect on the polymer network, thus decreasing gel strength.

Presently, one of the most challenging aspects of applying oleogels to food systems is the difficulty in accurately mimicking the textural properties of traditional fats. In this regard, EC oleogels appear to show great potential. The influence of surfactants on these gels has been well documented, and may provide one means to modify textural properties [19,23[•]]. In addition to enhancing gel strength, increasing the polarity of the oil phase can completely eliminate oil loss upon deformation and



(a,b) Mechanical strength of EC oleogels with additives to modify solvent quality (ϕ_s indicates the mass fraction of the oil phase replaced). (a) Influence of castor oil (open circles) and mineral oil (filled diamonds) on gel strength. (b) Effect of oleic acid (filled circles) and oleyl alcohol (open triangles). Fitted parameters F_{rel}^{max} and K_d represent the maximum relative force and the Langmuir dissociation constant, respectively. (c) Interaction distance between ethylcellulose and blends of soybean oil/castor oil, according to Hansen solubility theory: solid line: full formalism ($R_{j,k}$); dashed line: hydrogen bonding parameter only. (d) Zero shear rate viscosity of ethylcellulose in soybean oil/castor oil blends. Viscosity measured at 150 °C to avoid influences of gelation. Source: Adapted from Gravelle et al., 2015 [26**].

greatly increase the elasticity of these gels. Similarly, the presence of oleic acid or oleyl alcohol can also eliminate oil expulsion and improves elasticity and resilience. The ability to mimic both the functional and textural attributes of hard-stock fats would be a large step forward in the field of oleogelation, and presently such strategies are actively being explored.

Plant-based wax oleogels

Natural plant-based waxes gel liquid oils at concentrations as low as 1–4 wt% by forming a three-dimensional network that entraps oil within its pores and by adsorbing oil onto the surface of the network [9,30–33]. Rice bran wax (RBX), candelilla wax (CLX), and carnauba wax (CRX) have been given GRAS status by the US FDA. They are therefore promising oil structuring agents because they are commercially available and relatively inexpensive considering the amount required for gelation. The rheological properties of wax oleogels can be matched with that of PHOs depending on the type and concentration of wax, and by utilizing various processing conditions. Wax oleogels are formed by heating wax-oil mixtures above the melting range until the wax particles are fully dissolved, followed by subsequently cooling the melt, either statically, or under shear [11[•]]. The morphology and aggregation of the three-dimensional structure of wax oleogels are determined by the chemical composition of the waxes, concentration employed, and processing conditions, such as shear and cooling rate [31–37].

The oil-binding properties of RBX, CLX, CRX, and sunflower wax (SFX) have been examined by a few research groups $[31-34^{\circ},36,37]$. As shown in Figure 3, these four plant waxes form different crystal microstructure in canola oil, and the critical gelation concentration (C_g) of RBX, SFX, CLX and CRX were 1, 1, 2, and 4 wt% [31,33]. The oil binding capacity of these plant waxes was shown to be directly affected by the crystal morphology and the organization of the three-dimensional network, where a higher oil-binding capacity was associated with an even distribution of mass and larger crystal size [31,33]. Among these four plant waxes, CLX oleogels exhibited the highest oil binding capacity [31]. The





Bright field light micrographs of wax organogels consisting of canola oil and rice bran wax (a), sunflower wax (b), candelilla wax (c) and carnauba wax (d) at relatively high concentrations of 10% (w/w). Source: Adapted from Blake and Marangoni, 2015 [31].

three-dimensional network of CLX oleogels had the smallest crystals and lowest spatial distortion, characterized by the highest fractal dimension, resulting in a higher surface area, leading to smaller pores which are able to more efficiently immobilize the oil phase (Figure 3c) [31]. In addition to the structure and concentration of plant waxes, minor components naturally present in wax and the chemical nature of the oil phase was found to modify the microstructural morphology and thermal and rheological properties of these gels [31,36–38°]. For example, a comparatively lower concentration of wax is required for gelling vegetable oils that have a lower degree of unsaturation [36].

External factors, including shear and cooling rate, affect the crystal morphology and oil-binding capacity of wax olegels in a complex way. As a result, controlled, shearinduced microstructural changes provide a means to tailor the oil binding capacity of these oleogels, based on the type of wax employed [32,34°,39]. For example, the application of shear increased the oil-binding capacity of RBX gels under slow cooling rates by creating a tortuous network of loosely bound oil, whereas shear decreased the oil-binding capacity of CLX gels by promoting the formation of larger crystals resulting in reduced surface area. Therefore, RBX would be a more appropriate gelator for processing conditions involving shear [34[•]].

Due to the versatility and thermal reversibility of plant wax oleogels, their use has been explored in several different food applications, such as fat reduction in icecream (RBX), cookies (SFX), margarine (SFX oleogels and emulsions) as well as other food systems [40–42]. When applying wax olegels in food systems, the presence of water could interfere with the structure of oleogels, therefore emulsion systems incorporating wax oleogels may become an intergrade alternative structuring strategy [35°,42].

Structured emulsions

Structured emulsions are another systems that have been shown to be promising alternatives to PHOs, as they can be formulated to have a solid-like structure similar to that of hard-stock fats [43]. Monoglycerides (MGs) are commonly used food emulsifiers that self-assemble into lamellar, cubic or hexagonal phases in both hydrophobic and hydrophilic systems [44–48]. MGs form structured oil-in-water emulsions when the system contains greater than 10 wt% but less than 70 wt% oil [49,50]. These MG-structured emulsions have been shown to be an effective low fat alternative for PHO-based shortenings [34°,49,51].

MG-structured emulsions are prepared by adding the oil phase (liquid oil, MGs, and co-emulsifiers) into the water phase (water, preservatives, and polysaccharides) using a low energy emulsification process [49]. Before homogenization, the oil phase and the water phase must be heated above the Krafft temperature (T_{k}) to melt the hydrocarbon chains of the MG molecules [50]. Upon homogenization, the oil phase is added to the water phase, provoking the MG molecules to self-assemble into an L_{α} liquid crystalline phase [50]. When the system is subsequently cooled below T_k , the hydrocarbon chains of the MG molecules lose their mobility, initiating a transition to the L_{β} phase (i.e. the α -gel phase) [52,53]. The resulting emulsions have an onion-like structure consisting of an oil droplet surrounded by alternating MG bilayers and water (Figure 4a) [54]. The hydrated lamellar structure of the α -gel phase has a fat-like texture, making these structured emulsions ideal substitutes for products such as margarines (see Figure 4b) [50,55,56]. Furthermore, as the stabilized oil droplets are essentially encapsulated by the concentric MG bilayers, it is possible to incorporate various lipophilic nutrients in the oil phase [49.57–59].

The difficulty in using MG-structured emulsions is that the α -gel phase is thermodynamically unstable and upon aging, it will undergo a polymorphic phase transition into a more densely packed coagel phase, reducing the space between the MG bilayers, and resulting in water expulsion (Figure 4c) [52]. The water-swelling capacity of the α -gel phase can be enhanced by incorporating negatively charged co-emulsifiers into the MG-bilayers. These co-emulsifiers improve the α -gel stability by increasing the electrostatic repulsion between bilavers to increase water laver thickness, disrupting the polymorphic phase transition as a block unit in the highly organized MG molecules of the bilayer structure [55,56,60,61[•]]. Sodium stearoyl lactylate (SSL) are negatively charged molecules which naturally crystallize in the α form, and therefore function as an effective co-emulsifier in MG-structured emulsions to slow down the transition into the coagel phase [62]. Increasing the concentration of SSL in MG up to 20 wt% has been shown to stabilize the α -gel phase up to two months under accelerated shelf life tests [61[•]]. Other factors such as pH and ionic strength also need to be taken into consideration when formulating these structured emulsions in order to form a stable α -gel phase [56,63[•]]. In terms of processing conditions, slow cooling rates have been shown to improve the stability of the α gel phase by providing more time to form fully hydrated lamellar structures, while shear accelerates this polymorphic transition by disrupting the formation of hydrated lamella [54,61,64,65]. Storage under refrigeration temperatures has also been shown to delay the polymorphic transition of MG-structured systems and achieved α -gel stability for over three months [66[•]].

MG-structured emulsions can be tailored to exhibit a wide variety of textures and mechanical properties for bakery products such as cookies and puff pastries [35^{••},51]. The unique architecture of these structured emulsions makes it possible to incorporate various types of liquid oils to the system without dramatically altering the rheological properties [49,57,58]. Several other co-emulsifiers, such as sodium stearate, diacetyl tartaric acid





(a) Architecture of MG-structure emulsion; (b) an emulsion in the α -gel phase of the MG-water system where thick layers of water are structured between concentric MG bilayers; and (c) coagel phase in which the MG-molecules become tilted and more densely packed in the bilayers and reducing their ability to retain water.





Schematic diagram of a MG-based structured emulsion, adapted from Blake and Marangoni, 2015 [35^{••}]. The textural and functional properties of these emulsions can be tailored by structuring the oil phase, either by incorporation of fats or non-traditional structuring agents, such as plant-based waxes and polymeric organolgelators.

ester of mono and diglycerides, lecithin and phospholipids have also been identified which stabilize the α -phase, and can be selected based on the pH and formulation requirements [56,59,61°,67–70]. Finally, one of the most promising aspects of MG-structured emulsions is the ability to tailor their rheological properties, either by adjusting the MG chain length, or by introducing organogelaters or palm fats to the oil phase to enhance laminating properties (Figure 5) [13,35°,42,49–51,58].

Concluding remark

A successful approach to the replacement of *trans*-fat with alternatives will involve the combination of several strategies, such gelled oil within structured emulsions and/or combination of oleogelators, in order to achieve the desired functional properties. One such example is shown in Figure 5 where oil gelled with waxes is entrapped within an emulsion structured with monoglyceride hydrated multilayers.

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