Advances in edible oleogel technologies – A decade in review

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ABSTRACT

Trans and saturated fat replacers/substitutes have been a tremendously active area of research for the food industry. Unlike polymers used for hydrogels, oleogels utilize small, amphiphilic molecules that self-assemble via highly specific, non-covalent interactions entrapping liquid oil via capillary forces. Edible applications of oleogels have replaced the need for trans unsaturated and saturated fatty acids to structure processed foods. These innovations mitigate the use of hardstock fats that are associated with deleterious health risks and negative consumer perception. Over the past decade, oleogels have made significant strides towards emulating desired sensory traits while maintaining healthy nutritional profile of the oil. Due to the rapid advancements in the past decade, the most promising technologies will be reviewed.

1. Introduction

Saturated and trans fats are perceived negatively due to their links to cardiovascular disease and other undesirable health effects (Aro, Juhaiainen, Partanen, Salminen, & Mutanen, 1997; Ascherio et al., 1994; Isomaa et al., 2001; Rogers, 2009; Stender, Astrup, & Dyerberg, 2012, 2014). These hardstock fats provide desirable functionality, texture and palatability. It is the hardstock triacylglycerols (TAGs) that form the fat crystal network comprised of crystalline lamellae that stack into crystalline nano-platelets (CNPs) (Gravelle, Davidovich-Pinhas, Zetzl, Barbut, & Marangoni, 2016). CNPs aggregate into flocs that entrap liquid oil within the solid fat network (Gravelle et al., 2016; Marangoni, 2012). However, lipids responsible for the elastic nature of fats are also the same fats associated with adverse chronic health effects. The adverse health outcomes associated with consuming these fats have led regulatory agencies to enact legislature banning industrial oils previously used in food systems, require other external factors to drive self-assembly such as pH, light, and solvent changes (Terech & Weiss, 1997; van Esch, 2008; Weiss, 2014; Weiss & Terech, 2006). Highly effective oleogelators form gels in apolar liquids at concentrations as low as 0.5 wt% (Hughes et al., 2009). This ability to structure oleogels at low concentrations is appealing to the food industry. Oleogels, despite being in their early stages of development for food applications, have been widely studied in both the cosmetic and pharmaceutical industries (Bastiat & Leroux, 2009; Kantaria, Rees, & Lawrence, 1999; Patel & Velikov, 2011; Prausnitz, Mitagrotri, & Langer, 2004; Vintiloiu & Leroux, 2008). Applications of oleogels in foods are limited because of the difficulty in identifying food grade, inexpensive gelators. Even with this limitation research has increased exponentially, illustrating the vast interest garnered by oleogels. This paper examines the most promising oleogel systems presented over the past decade and their edible applications. Readers are also directed to other seminal reviews on oleogels (Co & Marangoni, 2012; Dassanayake, Kodali, & Ueno, 2011; Marangoni & Garti, 2011; Rogers et al., 2014).

Oleogels self-assemble, in apolar solvents, via non-covalent interactions forming fibrillar or platelet crystals (Patel & Dewettinck, 2016; Rogers, 2009). The interactions responsible for gelation include hydrogen bonding, π-π stacking, electrostatic and van der Waals interactions (Oksesola, Vieira, Cornwell, Whitelaw, & Smith, 2015). These interactions favor 1-dimension (1D) growth and these 1D fibers form junction zones linking numerous 1D structures forming 3-dimensional (3D)
networks.

2. Alternative oil structuring strategies

Numerous approaches to oil structuring exist (Fig. 1) with the most common alternative structuring method to colloidal fat crystal networks being the direct dispersion of a gelator into liquid oil. Direct dispersal of gelators includes: lipid-based, ethylcellulose (EC) and colloidal silicon dioxide (CSD). Lipid-based gelators are subdivided into waxes, fatty acids and monoglycerides (Patel & Dewettinck, 2016). To achieve gelation, following dispersal of the gelator into the oil phase, the resulting sol is often cooled to induce nucleation and crystal growth, leading to the formation of self-assembled networks (Patel & Dewettinck, 2016). Indirect methods require the formation of structural framework in an aqueous solvent or water continuous emulsion (Adelmann, Binks, & Mezzenga, 2012; Mezzenga & Ulrich, 2010; Whitby & Onnink, 2014). The gel network must be conserved during the careful removal of aqueous solvent. The use of oil sorption involves the enrichment, in this case by oil, of a porous material leading to an increased density (Rouquerol, Rouquerol, & Sing, 1999). Absorbent fillers have already been employed in foods in order to contain moisture and adjust product parameters such as consistency, flowability, and texture (Patel & Dewettinck, 2015).

Monocomponent gels utilize a single gelator to structure liquid oil and mixed gels require synergistic interactions between multiple gelators (Pernetti, van Malsen, Floter, & Bot, 2007). Mixed system gelation is influenced by heterogeneous nucleation, increased nucleation rate, and network strengthening (Patel & Dewettinck, 2016). Mixed component gelation is found in wax-based oleogels due to variable components and ratios of natural waxes (Patel & Dewettinck, 2016). Oleogelators often require additional processing or processing aids before gelation is achieved; for example, EC is poorly soluble in oil and must be heated above its glass transition temperature (140 °C) in order to achieve uniform dispersion (Patel & Dewettinck, 2016). While for CSD, high shear must be applied to disrupt aggregate formation, allowing uniformed dispersal of small aggregates that form a continuous network (Patel, Mankoč, Bin Sintang, Lesaffer, & Dewettinck, 2015).

3. Waxes & shellac

Wax gelators are comprised of varying fractions of n-alkanes, fatty alcohols, and fatty acids depending on the origin of the wax and the proportions of these constituents have a critical role on gelation. Wax esters form platelet-like or needle-like crystals in edible oils at low concentrations compared to TAGs and they do not have negative health detriments (Toro-Vazquez et al., 2007). Candelilla wax (CDW), carnauba wax (CBW), rice bran wax (RBW) and beeswax (BW) are of great interest as food-grade waxes for use as edible oleogels (Lim, Hwang, & Lee, 2016; Toro-Vazquez et al., 2013; Toro-Vazquez, Morales-Rueda, Mallia, & Weiss, 2010; Toro-Vazquez et al., 2007; Zulim Botega, Marangoni, Smith, & Goff, 2013). CDW, sourced from the leaves of Euphorbia cerifera, is composed of n-alkanes, between 29 and 33 carbons and structures safflower and canola oil at concentrations of 1 wt% and 2 wt%, respectively (Blake, Co, & Marangoni, 2014; Instituto de la Candelilla, 2004; Toro-Vazquez et al., 2007). BW oleogels, compared to CBW and CDW oleogels formed in canola oil, have superior adhesive and cohesive properties (Table 1) (Lim et al., 2016). CDW is typically the most elastic (i.e., highest hardness value) and BW is the lowest (Lim et al., 2016). Oleogels comprised of BW,
CBW, and CDW reduced peroxide value compared to pure canola oil (Lim et al., 2016).

Plant waxes, such as CDW and CBW, form ‘needle-like’ crystals (Blake et al., 2014; Dassanayake, Kodali, Ueno, & Sato, 2009). Previously, it was believed that ‘needle-like’ crystals were required to form the entangled network to bind oil. More recently, the morphology of the wax crystals of sunflower wax (SW), RBW and CDW were reported as platelets (Blake & Marangoni, 2015). These findings align with observation made in mineral waxes, which have been reported as ‘platelet-like’ morphologies (Miyazaki & Marangoni, 2014). Additionally, the dimensionality of ‘needle-like’ structures, observed on optical light micrographs, matched observations of the platelets observed through cryogenic scanning electron microscopy (Blake & Marangoni, 2015). Further, nanoplatelets are on the same nanoscale order of magnitude as the nanoplatelets observed in fat crystal networks (Hwang et al., 2015).

Shellac is a resin purified from secretions of the insect Laccifer lacca and has had a long history of uses in pharmaceuticals, cosmetics and foods applications (Patel, Schatteman, De Vos, et al., 2013; Patel et al., 2014). Shellac has properties congruent to those of an oleogelator in that they are lipophilic, have the ability to self-assemble, and are thermoreversible (Patel, Schatteman, De Vos, et al., 2013). Shellac structures edible oils at concentrations as low as 2 wt% and may do so in the presence of water. Water-in-oil emulsions were stable for longer than 18 weeks when shellac was added at concentrations as low as 1.6 wt% (Patel, Schatteman, De Vos, et al., 2013). The rate of cooling greatly alters the crystallization kinetics and resulting crystal network formation (Fig. 2). Slower cooling rates delayed the onset of nucleation and crystal formation, resulting in larger, less dense crystals (Patel, Schatteman, De Vos, et al., 2013). The resulting crystal network led to weaker oleogels compared to the same blends cooled at faster rates (1°/min vs. 10°/min) (Patel, Schatteman, De Vos, et al., 2013). It is believe the increased surface area of smaller crystals creates increased opportunity for crystal-crystal interactions resulting in a strengthened crystal network (Patel, Schatteman, De Vos, et al., 2013).

4. Ethylcellulose

EC is derived from cellulose where hydroxyl groups have been ethylated and the degree of substitution (DoS) determines its solubility, (i.e., 1.0 < DoS < 1.5 soluble in water; 2.4 < DoS < 2.5 soluble in organic solvent). Typically, EC has a DOS of ~2.5 (Fig. 3) (Davidovich-Pinhas, Gravelle, Barbut, & Marangoni, 2015; Koch, 1937). EC has applications in plastics, ceramics, coatings, pharmaceuticals, cosmetics and as a food additives (Davidovich-Pinhas et al., 2015; Hughes et al., 2009; Knill & Kennedy, 1998; Koch, 1937; Rekhi & Jambhekar, 1995; A. K. Zetzl, Marangoni, & Barbut, 2012). EC is relatively inexpensive, commercially available and food grade (Zetzl et al., 2014). Until recently, EC has been the only polymer applied as an edible oleogelator; however, hydroxypropyl methylcellulose also has similar oil structuring properties (Patel, Schatteman, Lesaffre, & Dewettinck, 2013; Zetzl et al., 2014). EC, upon addition to the oil, must be heated above its glass transition and
subsequently cooled to return the polymer into a rigid state forming intermolecular interactions via hydrogen bonding to produce an entangled network that entraps the oil (Gravelle, Barbut, Quinton, & Marangoni, 2014; Laredo, Barbut, & Marangoni, 2011). Gravelle et al., 2014 correlated the mechanical properties of EC oleogels with the mass fraction of EC, mass fraction of surfactant, EC molecular weight, oil type, surfactant type and EC/surfactant ratio (Gravelle et al., 2014). The setting temperature for gelation of EC oleogels was found to influence the gel strength (i.e., higher setting temperatures formed more ordered cross-linked polymer chains) (Davidovich-Pinhas et al., 2015). Conversely, when the setting temperature was at lower temperatures, hydrogen bonds formed more sporadically leading to a less ordered weaker network with reduced hardness and fracture force (Fig. 4). EC oleogels were more elastic when surfactants were incorporated into the gel structure (Davidovich-Pinhas et al., 2015).

The mechanical properties of edible EC oleogels change depending on the type of oil being used. The parameters of the oil which influence the mechanical properties include: molecular weight, TAG composition, polar oxidation products and surface-active molecules (Gravelle et al., 2016). Solvent polarity was correlated to the mechanical behavior of EC oleogels, which was attributed to polar functional groups interfering with EC interactions. The presence of small, surface-active molecules with the ability to hydrogen bond, such as oleic acid and oleic alcohol in small proportions (< 0.5%), resulted in a significant increase in gel strength (Gravelle et al., 2016). Gel strength was measured through NMR T2 relaxation times, shorter pulsed reaction times were indicative of more restricted mobility of solvent and thus a stronger gel (Gravelle et al., 2016).
The ability of EC to form an oleogel depends on the ability to hydrogen bond, forming a 3D network from 1D polymer strands. Hydrogen bonding also aids in determining the gelator solubility. To quantify the importance of hydrogen bonding to solubility, castor/soy oil-based-EC systems were made at various concentrations of EC and Hansen solubility parameters (HSP) were calculated and correlated to shear rate-dependent viscosity which is an indicator of polymer/solvent interaction (Gravelle et al., 2016). Castor oil was selected as one of the solvents due to its polarity; 85% castor/soy oil-based-EC system was found to form the optimal oleogel (Gravelle et al., 2016). This ratio exceeds the 60% castor/soy oil-based-EC oleogel composition predicted by HSP parameters to be the optimal solubility for the EC oil blend (Gravelle et al., 2016). This reveals not only is hydrogen bonding important in oleogel system solubility, but also reinforces the glaring need for well-developed encompassing formula to predict optimal gel solubility.

5. Templating polymeric oleogelators

Most food polymers are hydrophilic in nature and are not their dispersible in oil making them ineffective gelling systems. However, systems containing water as the continuous phase in emulsions may be used as a templates to gel the dispersed oil (Patel & Dewettinck, 2016). For example, EC polymers are pre-hydrated initiating polymer-solvent interactions as well as forming physical crosslinks between polymers. This gels the aqueous phase, which is then dehydrated carefully to preserve the conformational framework of the polymer network entrapping the dispersed liquid oil. Indirect dispersion utilizes the framework created at oil-water interfaces and following the removal of water, leaves oil entrapped in the 'dried' microstructural network (Adelmann et al., 2012; Mezzenga & Ulrich, 2010; Whitby & Onnink, 2014). Using water continuous emulsions as templates can create oil powders, gels and soft solids that can structure very high concentrations of oil with minimal oil leakage over prolonged storage periods (Patel et al., 2015).

Porous additives hold some beneficial traits for aiding in structuring oils. Sorption techniques are used in many field such as pollution control and catalysis. The recent usage of newly developed porous materials to help clean up oil spills can be applied to structuring oils (Patel & Dewettinck, 2016). Hydroxyl propyl methylcellulose was used to stabilize an aqueous foam as a template to adsorb oil (Patel, Schatteman, Lesaffer, & Dewettinck, 2013). The incorporation of hard-stock fats, at a 5 wt%, to this template improved the thixotropic recovery properties (Patel & Dewettinck, 2015). The sorption process results in the increase in the density of a material through physical interactions at an interface. Preliminary studies have shown that porous cellular structures could be quite effective, absorbing 100 times its own weight and containing up to 98 wt% liquid oil (Patel & Dewettinck, 2015).

6. Ceramides

Ceramides are a class of polar lipids characterized by the presence of a sphingosine base, which contains an 18-carbon unsaturated aliphatic chain and a fatty acid (Fig. 5). Sphingosine-derivatives, such as ceramides and sphingolipids, play an important role in cell signaling and regulate integral aspects of cell development including: differentiation, proliferation, and apoptosis (Ogretmen & Hannun, 2004). As an oleogelator, some ceramides can structure oil reducing the need for trans and saturated to structure oil and they have positive health benefits. Ceramides reduce total serum cholesterol by 30% and improve the serum lipoprotein profile (Kobayashi, Shimizugawa, Osakabe, Watanabe, & Okuyama, 1997). Ceramides induce apoptosis by promot-

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Fig. 7. Polarized light (Top) and brightfield (Bottom) micrographs of a 5% wt (1% Stearic acid and 4% Cholesterol) mixture in canola oil. Scale bar represents 500 μm. Adapted from Wang & Rogers. Biomimicry - An approach to engineering oils into solid fats. Lipid Technology, 2015, 27, 175–178 with permission from John Wiley and Sons.

Fig. 8. Structure of β-sitosterol and γ-oryzanol.
ing production of interleukin 1B and regulate apoptosis regulating tumor cell growth (Wang & Rogers, 2015). Ceramides have a role in inhibiting carcinogenesis of colon cancers, attributed to its effects on cell differentiation, growth, and apoptosis (Wang & Rogers, 2015). C2 in particular has been shown to decrease cell viability of colon prostate, ovarian, and leukemia cell lines, while longer fatty acid chain counterparts are ineffective (Rogers, Spagnuolo, Wang, & Angka, 2016).

Individually, most ceramides are poor gelators, with the exception of short-chain ceramides, for example N-acetylo-erythro-sphingosine (C2 ceramide) (Rogers et al., 2016). Increasing the fatty acid chain length adversely affects the ability of ceramide to gel vegetable oil and at 2 wt%, fatty acid chain length > 6 carbons do not gel. At 5 wt%,
organogels are observed beyond 6 carbons (Rogers et al., 2016). It has been reported that shorter fatty acid chain lengths promote fibril growth, whereas longer chain lengths promote spherulitic or platelet crystal morphologies (Wang & Rogers, 2015). Additionally, as fatty acid chain length increases so does melting temperature but it negatively correlates to the elastic modulus of the organogel (Rogers et al., 2016).

At low concentrations, long chain length ceramides (i.e., ceramide III), β-sitosterol and stearic acid are ineffective individual gelators. Stearic acid and ceramide III form platelets and β-sitosterol forms spherulites (Fig. 6) (Wang & Rogers, 2015). A dramatic difference in microstructure is observed when stearic acid and cholesterol are added in a 1:4 ratio to canola oil. Fibers result at the 1:4 ratio, highlighting the complexity and changes in structure that occur when varying the concentrations of multiple-gelators (Fig. 7) (Wang & Rogers, 2015). Despite forming fibers, which have limitations in food applications, both the cosmetics and pharmaceutical industries may find these useful. Oleogels derived from different ratios of stearic acid, ceramide III and β-sitosterol produce very different morphologies with very different physicochemical properties (Wang & Rogers, 2015). Further research in these ratios, find ideal combinations that are appropriate for edible applications.

7. β-Sitosterol and γ-oryzanol oleogels

Individually, neither β-sitosterol nor γ-oryzanol (Fig. 8) self-assemble efficiently enough to entrain oil. When combined at a 60:40 wt% γ-oryzanol/β-sitosterol ratio (or a 1:1 M ratio) they form hollow tubules at concentrations as low as 2%, less resulting in a strong oleogel (Bot et al., 2012; Moschakis, Panagiotopoulou, & Katsanidis, 2016; Rogers, 2009). To form gels several criteria are required for this system listed in decreasing order of importance: synergistic hydrogen bonding, a ring system, and alkyl residue (Bot & Agterof, 2006). Although the co-crystallization of β-sitosterol with γ-oryzanol is the most widely studied phytosterol co-crystal, other plant sterols such as ergosterol, stigmasterol, cholesterol, cholestenol form similar structures with varying tubule diameter and wall thickness (Bot et al., 2012). Small-angle X-ray scattering (SAXS) determined that tubule diameters were between 67 and 80 Å, wall thickness was between 8 and 12 Å (Fig. 9) and tubule length exceeding 1000 Å (Bot et al., 2012). These multifaceted oleogelators are already deemed food grade (Zetzl, Marangoni, & Barbut, 2012) and phytosterols lower blood cholesterol levels and contribute satiety making these attractive alternatives to colloidal fat crystal networks (Hughes et al., 2009; Rogers, 2009). In sunflower oil, oleogels are transparent and by varying the sterol type and concentration, the mechanical and rheological properties of the oleogel can mimic saturated fats (Panagiotopoulou, Moschakis, & Katsanidis, 2016), β-sitosterol and γ-oryzanol also modify volatile molecule release (Chen et al., 2017).

The ratio between γ-oryzanol, β-sitosterol and vegetable oil effects

**Table 2**

Gelation abilities of sugar amphiphiles in various organic solvents and oils and respective structures.

Adapted from Jadhav et al. Sugar-derived phase-selective molecular gelators as model solidifiers for oil spills. Angewandte Chemie, 2010, 49, 7695–7698 with permission of John Wiley And Sons.

<table>
<thead>
<tr>
<th>Liquid or oil</th>
<th>Man-4</th>
<th>Man-8</th>
<th>Sor-4</th>
<th>Sor-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut oil</td>
<td>G (4.0)</td>
<td>G (1.3)</td>
<td>G (5.0)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Olive oil</td>
<td>G (2.5)</td>
<td>G (1.0)</td>
<td>G (1.0)</td>
<td>G (1.5)</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>G (4.0)</td>
<td>G (1.3)</td>
<td>G (5.0)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Grape seed oil</td>
<td>G (4.0)</td>
<td>G (1.3)</td>
<td>G (5.0)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Canola oil</td>
<td>G (4.0)</td>
<td>G (1.0)</td>
<td>G (1.0)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Grilled sunflower oil</td>
<td>G (4.0)</td>
<td>G (1.0)</td>
<td>G (1.0)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>G (1.0)</td>
<td>G (2.5)</td>
<td>G (1.0)</td>
<td>G (2.5)</td>
</tr>
<tr>
<td>Triton</td>
<td>G (2.5)</td>
<td>G (1.5)</td>
<td>G (3.0)</td>
<td>G (2.5)</td>
</tr>
<tr>
<td>Propanol</td>
<td>G (2.5)</td>
<td>G (1.3)</td>
<td>G (0.25)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>G (2.5)</td>
<td>G (2.0)</td>
<td>G (3.0)</td>
<td>G (3.0)</td>
</tr>
<tr>
<td>Toluene</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Methanol</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Water</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>H202</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>H20</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Dextrose</td>
<td>G (2.5)</td>
<td>G (3.0)</td>
<td>G (3.5)</td>
<td>G (3.5)</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>G (1.2)</td>
<td>G (1.5)</td>
<td>G (1.5)</td>
<td>G (1.5)</td>
</tr>
<tr>
<td>Pbenzoil</td>
<td>G (2.0)</td>
<td>G (2.5)</td>
<td>G (2.5)</td>
<td>G (2.5)</td>
</tr>
<tr>
<td>Pphenyl</td>
<td>G (2.0)</td>
<td>G (2.5)</td>
<td>G (2.5)</td>
<td>G (2.5)</td>
</tr>
<tr>
<td>Silicone oil</td>
<td>G (4.0)</td>
<td>G (5.0)</td>
<td>G (5.0)</td>
<td>G (5.0)</td>
</tr>
<tr>
<td>Mixture of hydrocarbons</td>
<td>G (2.5)</td>
<td>G (3.0)</td>
<td>G (3.5)</td>
<td>G (3.5)</td>
</tr>
</tbody>
</table>

**Fig. 11.** HO and VOO oleogels prepared with BW and SW compared to commercially available butter and margarine. Reproduced from Yılmaz & Öğütçu. Oleogels as spreadable fat and butter alternatives: sensory description and consumer perception, RSC Advances 2015, 5, 50,259–50,267 with permission of The Royal Society of Chemistry.
the crystalline structures observed and their ability to entrain liquid oil (AlHasawi & Rogers, 2013). The ternary phase diagram (TPD) (Fig. 10) displays a wide array of ratios of γ-oryzanol, β-sitosterol, and canola oil which exhibit numerous polymorphic forms, melting points, and morphological characteristics (AlHasawi & Rogers, 2013). A mixed crystalline phase was observed at γ-oryzanol ratios between 30% and 100%, β-sitosterol levels between 0% and 20%, and canola oil between 0% and 70%. This region of the TPD required large supercooling to initiate nucleation, when nucleation occurred it was rapid, leading to numerous small crystals (AlHasawi & Rogers, 2013). Lamellar crystals formed having a spherulitic morphology. The large central region consists of 20%–70% γ-oryzanol, 60% - 10% β-sitosterol and 20% - 60% canola oil and forms a single crystalline phase, which seems ideal as a trans and saturated fat replacer. The TPD illustrates various polymorphic phases and microstructural elements that may be modified simply by altering the proportions of γ-oryzanol, β-sitosterol and canola oil (AlHasawi & Rogers, 2013).

8. Carbohydrate-based oleogelators

Most carbohydrate-based gelators are considered biocompatible (Grassi et al., 2011) leading to very little research on the safety of these oleogelators. Sugar alcohols, such as sorbitol derivatives aim to be low cost, efficient oil gelators in the presence of water. Dialkanoate derivatives of both D-sorbitol and D-mannitol showed differences in gelation ability between Man-4 and Sor-4 as well as Man-8 and Sor-8 (Table 2). This highlights the importance of chirality on gelation, as the only difference in chemical structure between D-mannitol and D-sorbitol are the orientation of the hydroxyl group on C2 (Jadhav, Vemula, Kumar, Raghavan, & John, 2010). The importance of hydrogen bonding is also stressed as the protected Man-8 was unable to gel oil. In the presence of water, the hydrophobic tails of Man-8 and Sor-8 encouraged the molecules to align in the oil phase resulting in gel formation (Jadhav et al., 2010). Carbohydrate-based oleogelators are thus far an under-researched area, with high potential in providing edible gelators, capable of structuring oil in the presence of water.

9. Edible oleogel applications

Oleogels have been investigated in a wide array of products that are high in either saturated or trans fats. Frankfurters, high in saturated fat, form solid-like, stable emulsions that are capable of retaining water. Organogel-based emulsions with γ-oryzanol/β-sitosterol were first investigated to formulate frankfurters (Panagiotopoulou et al., 2016). Sensory analysis showed no significant difference between the 20% backfat control and a 10% backfat combined with 10% sunflower oleogels (Panagiotopoulou et al., 2016). Interestingly, the organogel-structured emulsion at a 30:70 ratio (γ-oryzanol: β-sitosterol) was more elastic, gummy and chewy compared to the 60:40 ratio (γ-oryzanol: β-sitosterol) (Panagiotopoulou et al., 2016). Frankfurters made using β-sitosterol, γ-oryzanol and sunflower oil were a suitable replacer for the pork backfat (Panagiotopoulou et al., 2016). EC has also been used to reduce the saturated fat content of frankfurters (Zetzl et al., 2012). Cooked frankfurters with the beef-fat replaced with EC and various vegetable oils showed no significant differences in chewiness or hardness compared to the control products made with beef fat (Zetzl et al., 2012). The physical attributes of the frankfurter could be tailored by varying the molecular weight of EC, EC concentration and fatty acid

Fig. 13. Particle size in different ice cream formulations (A) and the meltdown rate of different ice cream formulations in a continuous freezer (white bars) and batch freezer (black bars) (B). Adapted from Zulim Botega et al. Development of formulations and processes to incorporate wax oleogels in ice cream. Journal of Food Science, 2013, 78, C1845–1851 with permission from John Wiley and Sons.
distribution of the vegetable oil (Zetzl et al., 2012). One advantage of EC oleogels in this application arise from the interconnected structure with 0.5 to 6 μm holes where the liquid oil was entrapped (Zetzl et al., 2012). Beeswax (BW) and SW oleogels made with hazelnut oil (HO) or virgin olive oil (VOO) have been investigated and assessed by a sensory panel with butter and margarine as a point of comparison (Fig. 11). BW and SW oleogels, made with either HO or VOO, have similar structural and thermal properties compared to commercially-available spreads (Yılmaz & Öğütçu, 2015). The hedonic traits of these edible spreads tested positively and ~50% of consumers ‘would buy or try once and then buy the oleogel products’ illustrating that consumers may accept the oleogel alternatives as a replacement of spreadable fats (Yılmaz & Öğütçu, 2015). The firmness of a 2–6% sunflower wax in soybean oil oleogel was similar to margarine containing 18–30% hydrogenated soybean oil in non-hydrogenated soybean oil; however, the melting point was significantly higher than the commercial margarine (Hwang et al., 2013). Replacing conventional shortenings into baked goods, such as cookies, increases the spread factor and reduces the snapping force (Jang, Bae, Hwang, Lee, & Lee, 2015). Therefore, oleogels provide desirable spreadability and the replacement of shortening with the oleogels may be used to produced cookies with soft eating characteristics (Jang et al., 2015).

Shellac, a food-grade resin and potential oleogelator, has many food applications including use in spreads, chocolate pastes, and cakes (Patel, Schatteman, De Vos, et al., 2013; Patel et al., 2014). Shellac oleogels made with rapeseed oil and water were acceptable substitutes for commercial shortening (Patel et al., 2014). Shortenings must provide the desired textural aspects of baked goods and if oleogels are to replace shortening they must not compromise certain attributes such as their ability to shorten gluten networks. Comparative sensorial parameters of the cake prepared with traditional shortening versus the shellac oleogels showed statistically significant differences in the cakes’ volume, cell size, moistness, stickiness, and sponginess and no significant difference was observed for the crumbliness (Patel et al., 2014). Shortenings, often used for their foamability, allow air to be incorpo- rated into the batter without separating which produces homogenous crumb giving rise to the tenderness of cakes (Patel et al., 2014). The crumb structure of a cake produced with a traditional shortening verses a shellac oleogel are similar in appearance (Fig. 12). Not only has shellac been used as a shortening alternative, but so have SW and BW in HO and these oleogels have been incorporated into cookies (Yılmaz & Öğutcu, 2015). Cookies made from an oleogel or a commercial shortening were comparable and the oleogel outperformed the traditional shortening with regard to the textural, compositional and hedonic traits. This is a prime example of the organogels’ potential to achieve uncompromised taste and texture with no trans and reduced saturated fats.

Ice cream, typically high in saturated fat, is an ideal candidate to have a portion of the milk fat replaced with wax oleogels (Zulim Botega et al., 2013). Botega et al. combined emulsifiers and wax oleogels and observed no significant differences in the fat globule size when 15% fat was either from the wax oleogel or milk fat (Fig. 13). The ice cream formula consisted of either 10 or 15 wt% oleogel (i.e., oleogel consisted of 10 wt% wax in high-oleic sunflower oil) (Zulim Botega et al., 2013). Ice cream made with 15 wt% RBW and glycerol monooleate was melt-resistant but less effective when formulated with dairy fat (Fig. 13) (Zulim Botega et al., 2013). RBW and EC soybean oleogels have been incorporated into cream cheese (Bemer, Limbaugh, Cramer, Harper, & Maleky, 2016). EC oleogels with skim milk, whey protein isolate and non-fat dry skim milk were coagulated for 14–16 h (Bemer et al., 2016). The oleogel cream cheese (OCC) samples had improved

![Fig. 14.](image-url) Reproduced from Bemer et al. Vegetable organogels incorporation in cream cheese products. Food Research International, 2016, 85, 67–75 with permission of Elsevier.
nutritional profiles compared to full-fat control, with a 90% reduction in saturated fat and 120% increase in unsaturated fat. Full-fat controls and OCC samples were found to have similar textural attributes in saturated fat and 120% increase in unsaturated oil. Full-fat controls and OCC samples were found to have similar textural attributes compared to the control, with a 90% reduction in trans fats.

There is still the need for new efficient, low-cost gelators compatible with specific processing conditions of respective products. EC has been found to have an excellent capacity to structure oils but in large scale operations is unfeasible to meet the high temperature required to disperse it in oil. Plant waxes provide ideal hedonic characteristic which are more comparable to traits provided by saturated and trans fats but problems arise in stability over extended periods. There is currently a distinct gap in knowledge in regard to identifying ideal ratios of ceramides, fatty acids, cholesterol, phytosterols in terms of structuring oils, crystal morphology and resulting suitability for edible applications. Carbohydrate-based gelators although extensively studied have had minimal research in the field of edible oleogels. Success over the last few years with edible applications of oleogels will continue increase interest and research in the field. Despite the serendipitous discovery of a oleogelators, increased research have discovered numerous applications and provided a more comprehensive view of the field.

References


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