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Current Opinion in Food Science

Perspective on oleogelator mixtures, structure design and behaviour towards digestibility of oleogels

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The concepts of either multi-component supramolecular gels or structures derived from oleogels have not yet been fully investigated to their respective potentials. The study of hybrid structures might cover technological points such as (i) how to vehiculate hydrosoluble and/or liposoluble bioactive components simultaneously? (ii) How could the framework of an oleogel contribute to a specific structure design strategy? (iii) How does oleogels' structure influence bioactivity during digestion? A deeper understanding of these issues widens the range of opportunities foreseen for oleogel applications in food matrices. This paper presents the most relevant developments in the field, including the role of ingredients on structured oil-based systems. The authors' perspective towards digestibility of oleogels and oleogel-derived structures is also addressed.

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Current Opinion in Food Science 2020, **35**:xx–yy

This review comes from a themed issue on **Food engineering and processing**

Edited by **Pedro ED Augusto**

https://doi.org/10.1016/j.cofs.2020.01.001

Introduction

Oleogelation has been used as an evolving and efficient physical approach to convert low-viscous non-polar fluids into elastic solids, due to the establishment of a 3D oleogelator network. Thus, a non-flowing condition is especially induced by surface and capillary forces, without modifying the chemical characteristics of the liquid oil [1,2]. It has been considered a promising oil-structuring technique for the creation of healthier solid fat replacers (oleogels). This hot topic has been driven by: (i) evidences of the harmful impact of saturated, *trans*-esterified or even inter-esterified fats on human health, which leads to a negative perception by the consumers [3,4]; (ii) regulatory actions to ban trans fats from food formulations [5]; (iii) concerns regarding the sustainable practices from palm oil producers [6] and (iv) possibility of modulation of lipid digestibility and bioactives delivery [7,8].

Solid fats show technological application as food texture modifiers, since the rheological and thermal behaviours of the crystalline structure can be tailored, thus providing compelling functional characteristics in a myriad of food systems. However, it is not just a matter of direct replacement of (semi) solid fat with structured liquid oils, since the maintenance of product quality must be revisited and meet the required quality patterns.

Usually in the case of crystalline oleogels, the structural hierarchy of fat crystal networks arises from the assembly of triacylglycerol molecules into nano-platelets at nanoscale. Further organizational events create crystal clusters and networks (microstructure) and finally bulk fat supplies the rheological properties, physical strength and sensory attributes at the macroscale. The manipulation of these macroscopic properties aiming at optimizing functionality can be guided by ingredient engineering [9]. When it comes to the number of oleogelators involved in the oil structuring process, the system can be defined as either a mono-component or a multi-component gel.

Hardly a monocomponent oleogel would be able to mimic properties that are commonly played by regular solid fats. Rather, the combination of gelators can modify functional arrangements of molecules, creating an enhanced gel network in which a large amount of liquid oil can be entrapped within the structure [6]. In addition, the use of indirect approaches (solvent exchange or emulsion template) may enlarge the possibility of using some polysaccharides and proteins as building blocks for oil structuring purposes. Moreover, the perspective of a single structure (oleogel) can be shifted towards that of a hybrid system, which results from a combination of different strategies.

The understanding of the foundation behind the design of food structures as a strategy for lipid delivery is an area of rapidly growing interest [10]. It is worthy to be explored, aiming at developing not only oleogels with

good stability and satisfactory bulk properties, but also oleogels that can effectively be incorporated in food matrices and provide additional health benefits. In this context, research on what occurs to oleogel systems in the digestive environment is a crucial step to evaluate the real potential of this technology within the food industry. The judicious modulation of lipid digestion by oleogels or oleogel-based structures opens up the opportunity of controlling bioaccessibility of lipophilic molecules that are able to be incorporated into them.

This review revisits the themes of ingredient and structure engineering related to oleogels. A better understanding of different levels of organization (from ingredient manipulation to structure) may guide the improvement of technological and nutritional aspects in a rational fashion. In nutrition, structured systems may be applied as bioactive compounds carriers, and they can also be used as a strategy to modulate lipid digestion. For these purposes, the fundamental science of ingredients and their interactions underpinning structure behaviour need to be unveiled along with the performance of oleogels or oleogels-derived systems under gastro-intestinal conditions through digestibility protocols.

Engineered oleogelator(s) network: multi-component systems formed by direct and indirect approach

Depending on the type of oleogelator, oleogels can exhibit a myriad of colloidal architectures, such as the networks of crystalline species, self-assembled fibrillar conformations, polymeric arrangements and 'indirect templated' systems [9]. Oleogels can be formed straightforwardly by mixing one component that shows suitable balance of solubility properties with oil medium (i.e. waxes; ethylcellulose; monoglycerides) applying temperatures above the melting point of the oleogelator. In contrast, oleogels can also be formed by means of a multi-step solvent exchange procedure, as applied, for example, to heat-set whey protein aggregates [11]. In such procedure, the polarity of the organic solvent is modified gradually by replacing the previous continuous phase for oil. For instance, solvents (e.g. acetone) that are capable of mixing with both water and oils can be applied; usually involving a two-step procedure to replace the water by the oil in the final system.

Depending on the nature of the structuring agents, the manufacture of tailored gels by combinations of different species of gelator molecules has been achieved from direct and indirect strategies that may provide distinguishing structural characteristics when compared to a monocomponent gel. Table 1 depicts some examples of multi-component gels achieved by different strategies, which rendered a number of differentiated technological and functional outputs.

An interesting and versatile ingredient in multi-component oleogelation is lecithin (LEC). The motivation in using it is usually twofold: i) it is a bio-based and ubiquitous ingredient and ii) according to its molecular structure, it can interact with different oil media, gelling and non-gelling additives by non-covalent interactions such as hydrogen bonds and van der Waals. Lecithin possesses a variable composition (phosphatidylcholine-PC, phosphatidylethanolamine-PE, phosphatidylinositol-PI and phosphatidic acid-PA) depending on its source and eventual modifications that can be performed (e.g. deoiled, enzyme modified, choline-enriched). This phospholipid has seen a widespread use as a surfactant agent and crystal habit modifier (changing crystal morphology of species) depending on food matrix, physical and colloidal state [12].

In multi-component systems, lecithin may play both main and co-oleogelator roles, depending on the formulation and type of lecithin. It has been used to structure vegetable oils as main gelator in the presence of trace amount of water (LEC: 99 wt% PC) [13] or with α-tocopherol [12] (LEC: 24 wt% PC, 20 wt% PE, 14 wt% PI and 8 wt% PA) as combined oleogelators to tune their molecular self-assembly. Within this approach, water (ranging from 0.25–0.9 wt%) or tocopherol (gelators were combined at 1:1 ratio) were responsible for the adjusted geometrical packing of the lecithin molecules, due to interactions between their polar regions, which induced the formation of cylindrical wormlike micelles [12,13].

Moreover, lecithin is a highly rated option applied to promote changes in the structure of a main oleogelator network. Some studies investigated lecithin's function as co-oleogelator, exerting control in the self-assembly of a host structuring agent, leading to an improvement of the gelation mechanism when applied simultaneously with sorbitan tristearate-STS (LEC: sunflower lecithin) [14], sucrose esters (LEC: sunflower lecithin) [15], fruit wax (LEC: soybean lecithin with 96.9 wt% PC) [16] and ethylcellulose (LEC: soybean lecithin with 20 wt% PC or 90 wt% hydrogenated PC) [17]. Different mechanisms were reported depending on the main gelator-lecithin combination. Lecithin acted by connecting the sorbitan tristearate crystals through weak junctions at LEC:STS ratios between 2:3 and 3:2 [14], while modifying the self-assembly of sucrose esters (SE) at 7:3 SE:LEC ratio by interrupting the extensive hydrogen bonds among SE monomers [15]. Likewise, the molecular assembly of fruit wax-FW (FW:LEC ratios of 3:1 and 1:1) or ethylcellulose (with addition of 1 wt% of LEC) was altered due to hydrogen bonding establishment between lecithin and the polar moieties of the corresponding molecules, respectively [16,17]. In contrast, a negative interaction took place by combining lecithin (LEC: egg yolk lecithin-96 wt% PC) with 12-hydroxystearic acid (12HSA) [18] which was related to the formation of intermolecular LEC-12HSA 1:1 complexes that caused structural

Table 1

Strategies to create oleogels (direct and indirect approaches) and oleogels-derived structures with different components combination

	Approach/strategy design	Components	Rationale	Ref.
Oleogel	Direct	I1) wax I2) β-carotene I1+I2: complex	Addition of functional (oxidative stability) and technological (improved mechanical properties) claims	[8]
	Direct	I1) ethycellulose I2) lecithin	Tailoring of ethylcellulose oleogels shear moduli: it increased 10-fold upon addition of lecithin	[17]
	Direct	I1) fruit wax I2) lecithin	Reduction of waxy mouthfeel and improvement of mechanical and thermal properties	[16]
	Indirect: emulsion-template freeze-drying	I1) tea polyphenol-palmitate particles I2) citrus pectin	Improvement of physical properties (reinforcement from the interactions and entanglements among polymers chains)	[24]
	Indirect: emulsion-template and drying	I1) soy protein I2) k-carrageenan I1+I2: nanocomplexes	Enable the use of hydrophilic proteins as structuring agents for hydrophobic liquids	[19••]
	Indirect: emulsion-template and drying	I1) quillaja saponin I2) sunflower oil I1+I2: coated nanodroplets	Tuning colour performance of oleogels by locating the compositions of food colorants in different sections of hierarchal architecture of HIPES	[23]
	Indirect: solvent exchange (Supercritical-CO_2) and drying	I1) κ-carrageenan templates I2) lettuce-filler addition	Evaluation of lettuce homogenate as inactive filler agent of template network submitted to freeze-drying, as alternative to supercritical-CO_2-drying (reduction of shrinkage)	[25]
Oleogel-derived structures	Structured lipid oleogels in alginate microparticles	S1) β-sitosterol and γ-oryzanol or sucrose stearate/ascorbyl palmitate oleogels (menhaden oil or structured lipid) S2) alginate microparticles	Encapsulation of oleogels in alginate microparticles to improve oxidative stability of the lipids and to reduce leaching of the microparticles internal phase	[35]
	Hybrid gels (or bigels)	S1) beeswax oleogel (MCT) S2) alginate hydrogel	Evaluation of ratio oleogel-in-hydrogel emulsified system on rheological and textural properties	[32]
	Oleofoams	S1) monoacylglycerol and native phytosterols oleogel (canola oil) S2) air bubbles	To provide structure to aerated food products from a mixture of gelators influencing foaming properties of whipped oleogels	[26••]
	Water-in-oleogel emulsion	S1) ricebran wax oleogel (canola oil) and glycerol monostearate S2) water	Tailoring rheological behaviour of W/O emulsions through oleogelation of the continuous phase	[28,29]
	Water-in-oleogel emulsion	S1) lecithin and stearic acid oleogel (canola oil) S2) water	Assessing changes in the primary structure (worm-like micelles and crystals) when an emulsion is formed from an oleogel	[31]
	Glycerol-in-oleogel emulsion	S1) β-sitosterol and γ-oryzanol oleogel (sunflower oil) S2) glycerol	Address the water instability (sitosterol hydrate crystals) inherent to sterols-based gels by using glycerol as the polar phase rather than water	[38]
	Oil-in-water emulsion	S1) rice bran wax oleogel (soybean oil) S2) water and whey protein isolates	Oleogelation of emulsified oil may affect *in vitro* intestinal lipid digestion	[39]

MCT: medium-chain triacylglycerol.

modifications in the fibrous network in the 12-HSA organogel hindering gel formation.

An important parameter when dealing with mixtures in oleogels' formulations is the ratio between gelator components. For instance, the excessive binding between lecithin and ethylcellulose molecules resulted in interferences in the polymer-surfactant organization, reducing the overall mechanical properties of the gels [17]. Likewise, an excessive amount of lecithin can hinder the SE

network development, due to extreme branching of the tubules that will disrupt the regular growth of micelles [15]. These findings shed light on how important it is to seek for the ideal ratio (considering the final application) between the structuring agents and their proportion with liquid oil.

Another interesting aspect in ingredient engineering is to explore components that may present both health and technological claims. Interestingly, it was found that by incorporating β-carotene in wax-based oleogels an enhancement in the oleogel mechanical properties was observed, disclosing both functional and structural roles of the carotenoid compound [8]. Besides that, the combination between γ-oryzanol and β-sitosterol also meets both functions —nutritional and technological — adding great value to food systems.

As aforementioned, a more elaborated multi-component strategy would be to investigate gel formation achieved by indirect approaches, combining components with potential interactions to develop a complex arrangement. Usually, protein-polysaccharide complexation is used to stiff the interface of concentrated oil-in-water emulsions (high internal phase emulsion- HIPE). Pairs of soy protein: k-carrageenan [19••]; whey protein isolate-low methoxyl pectin [20] or even the triad gelatin, tannic acid, and flaxseed gum [21] complexes have been applied for HIPE stabilization. Apart from complexation mechanism, other approaches have been used such as cross-linking (i.e. between β-Lactoglobulin and glutaraldehyde) [22] and colloidal particles absorption (i.e. quillaja saponin coated nanoparticles or tea polyphenol-palmitate particles) [23,24].

Finally, a stepwise solvent exchange route appears as another procedure to be explored in oleogel formation. For that, subsequent structures must be modulated from a hydrogel network, with an intermediate phase as alcohol-gel that is dried using supercritical CO_2 to turn it into an aerogel. This aerogel template is then let to absorb oil, creating oleogels. Alternatively, still from a primary hydrogel network, a cryogel is obtained after freeze-drying, converting the internal framework into something similar to an aerogel template [25].

Overall, oleogel formation with tailored mechanical and thermal properties can be achieved exploring different routes, either by a simple mixture of compatible oleogelators or more sophisticated combinations (complexes, nanoparticle/gels, conjugates or stepwise solvent exchange), thus evoking ingredient engineering to optimize oleogelation as technology for food architecture development.

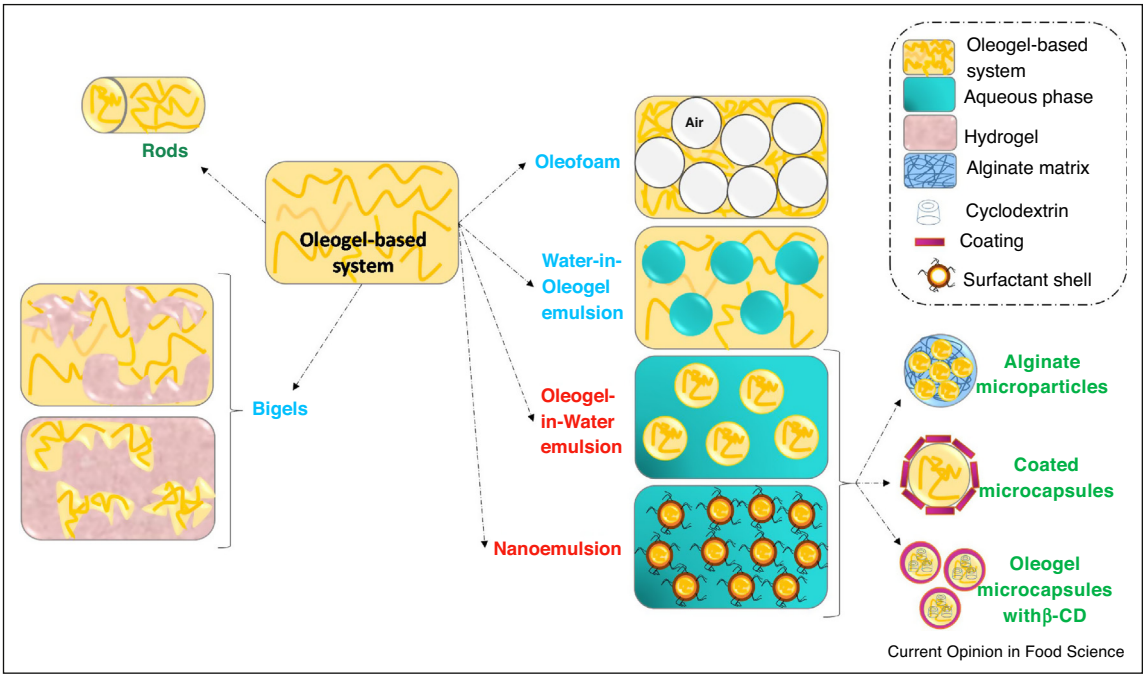
Oleogels as template for structure design: relationship between mixed-component oleogels' and their technological outputs

Oleogels are usually presented as a semi-solid bulk phase, which according to diverse purposes can be further modified following a design strategy. Possible routes would be the creation of more fluid boundaries (oleogel-in-water nanoemulsions or emulsions) or still keeping macroscopic bulk behaviour. Thus three possible different approaches can be related to generate oleogel-derived structures: i) maintenance of semi-solid texture profile (i.e. water-in-oleogel (W/O) emulsions, air-in-oleogel and hybrid hydrogel/oleogel systems); ii) manufacture of fluid-like systems (i.e. oleogel-in-water (O/W) (nano)emulsions); and iii) creation of shaped and compartmentalized structures (i.e. nano-particles and micro-particles, oleogel based rods) (Table 1). The latter category (iii) commonly involves a biphasic template from previous formation of an O/W (nano)emulsion (ii), as illustrated in Figure 1.

A myriad of technological challenges has been addressed based on oleogel-derived structures. In this way, the important aspect of elucidating and optimizing oleogels' behaviour in food matrices — dealing with the presence of water, mechanical energy involved in the manufacturing processes and interaction with other ingredients — may be a rationale to follow in exploring hybrid structures. Few papers have answered questions about how oleogels can induce structure in aerated foods [26••] or how this soft matter would behave while coexisting with water in real food systems [27••]. Table 1 and Figure 1 summarize some approaches to create oleogel-derived structures.

In the case of oleogel-inspired emulsions, micro-sized or nano-sized domains are dispersed in continuous phase, forming an interface in the presence of surfactant molecules, in which their nature along with volume fraction of (polar and lipid) phases may dictate whether a W/O or O/W emulsion is likely to be formed. Regarding water-in-oleogel (oleogelled) emulsions, their formation and settling properties can be achieved either by adding a surfactant or using another polar phase rather than water. The choice of surfactant can be delineated by modulating the interaction between this surface-active molecule and the oleogelator from the oleogelled continuous phase. Following this perspective, mechanical and thermal properties of rice bran wax (RBW)-based oleogels were manipulated in emulsions containing dispersed aqueous droplets either as inactive fillers [28] or crystal-stabilized droplets as active fillers [29]. In the former case, droplets were assumed to be inactive in emulsions stabilized by polyglycerol polyricinoleate (PGPR), since structure and stability of emulsions were mostly provided by the wax crystal network (oleogelator). Conversely, in the latter situation, droplets were considered active fillers, when glycerol monostearate (GMS) was applied as surfactant. Greater mechanical properties of emulsions were attributed to RBW-GMS interactions. In this case, wax crystals were mostly located in the continuous phase, whilst GMS crystals were interfacially bounded as a crystalline film surrounding the aqueous droplets. Thus, the strategy in these studies was to explore different surfactants in the perspective of ingredient engineering.

Figure 1



Schematic representation of engineered oleogel-derived structures. Systems are related to i) maintenance of semi-solid texture profile (blue), ii) manufacture of fluid-like systems (red) and iii) creation of shaped and compartmentalized structures (green).

In summary, PGPR worked by stabilizing the interface with no interaction with the continuous phase, whereas an additional structural mechanism was observed from combined RBX-GMS crystals forming solid shells surrounding water droplets [28,29]. Moreover, another strategy to address the eventual mismatch between oleogel and water phases (poor compatibility oleogel-water) would be to investigate whether water could be replaced by an alternative polar-liquid, such as glycerol, in order to ensure the dispersion of water droplets throughout the gel matrix [30].

An interesting aspect regarding oleogelled emulsions is the possibility to tune the self-assembly of oleogelators by creation of water-oil interfaces. For instance, in a multicomponent system comprises lecithin and stearic acid, the arrangement of oleogelators in oleogel (with no water) or in oleogelled emulsions was driven by the presence (or not) of water-oil interfaces. The primary dominant structure in oleogels was the entanglement of self-assembling lecithin worm-like micelles and the secondary structure was stearic acid (SA) crystals. Conversely, in the presence of water droplets, texture properties of emulsions were mainly provided by SA crystals, which interacted synergistically with the lecithin reverse micelles' network [31].

Besides oleogelled emulsions, other systems meet the objective of searching for structuring materials as candidates to replace solid fats in foodstuff, are the air-in-oleogel and hybrid hydrogel/oleogel systems. Whipped oleogels are oil foams obtained by whipping. A number of low fat aerated food products could be obtained via oleogelation based on air-in-oleogel structure [26••]. In turn, bigels or hybrid gels are formed from a mechanical mixture between hydrogels and oleogels in a balanced combination. Besides being an appealing texture modifier, bigels appear to be a promise vehicle for bioactive compounds [32].

Therefore, oleogel-derived structures are applied to tackle technological issues such as provision of different textures to the systems [31]. However, they can also be explored to address nutritional-related challenges, such as solubilisation of lipophilic compounds [33••]; modulating of oleogel behaviour towards *in vitro* digestibility (free fatty acids release) [7]; improvement of oxidative stability of bioactive compounds [34]; inhibit leaching of the internal phase during storage of microencapsulated products [35] among others. These functions can be obtained by manipulating bulk oleogels in different conformations such as to produce alginate microparticles using internal gelation method [35], WPI-covered particles by spray drying [36], or as cylindrical rods obtained from extrusion [37].

The routes for the formation of oleogel-derived structures can range from a simple mixing/homogenization, as for oleofoams and emulsions, up to elaborated strategies. In this approach,

usually a biphasic system (oleogel-in-water) is involved, intermediating particles' formation. Following the concept of more sophisticated structures, a multi-compartment system comprised β-cyclodextrins (β-CD) complexation with fish oil was incorporated in an oleogel structure and further emulsified and coated with a layer of whey protein isolate (WPI). Another example is the promotion of internal structuring and surface coating through creating an oleogel microparticle covered with a biopolymer. Both strategies were proposed as architectural templates to inhibit or delay oil oxidation and mask undesirable flavours [34,36]. Moreover, oleogel-derived microparticles were applied as strategy to prevent the leakage of bioactive compounds during storage and influx of pro-oxidative compounds into the alginate microcapsules formed by the double emulsion method [35].

Finally, a noble reason for designing oleogel-derived structures such as an oleogel-in-water is the possibility of modulating lipid digestion. Thus, the following section will cover this hot-topic in the perspective of oleogelation.

Oleogels seen as an opportunity to tailor lipid digestibility of bioactive compounds

As aforementioned, oleogels can be applied as a means to obtain a tailored nutritional profile. The backbone of the selected oil, which is the main constituent of the oleogel, is certainly decisive for the fatty acid profile of the final food product with incorporated oleogel. The increasing portfolio regarding to the molecules that are able to be applied for oil structuring purposes, makes oleogel structures as versatile as any other food structuring ingredient. Oleogels exert structural and textural functionalities, but can affect shelf-life behaviour or even the mouthfeel and flavour of certain products. Detrimental dietary practices are associated to disorders like metabolic syndrome, endothelial dysfunction, coronary heart disease, inflammation and others [40]. Healthier diets are a source for prevention or even treatment of some of these illnesses and an impactful way to enforce this is through the ingestion of foods enriched with functional compounds such as carotenoids, polyphenols or phytosterols.

Oleogels and oleogel-based structures can be used for the delivery of bioactive molecules [33••]. Oleogels are primarily constructed from a network of gelator molecules in oil medium that will assure the integrity of their configuration, standing as feasible vehicles of lipophilic ingredients. In contrast, oleogel-based structures like emulsion gels (hybrid gels) or bigels are able to serve both purposes of incorporating lipophilic and hydrophilic ingredients [41]. Gel network density, loading capacity, texture and rheological properties are among the most important features when considering viscoelastic matrices for carrying bioactive compounds. A number of edible oleogels have been studied and further characterized in the past decade; however, only a few have been handpicked for application as vehicles for selected bioactive compounds.

Different oleogelators are available, from small molecules that form colloidal or fibrillar networks through crystallization processes, to polymers (hydrophobic) that are able to self-assemble under specific processing conditions. The structure of a food product is directly linked to its digestibility and consequently to the bioacessibility of the incorporated nutrients. This could be explored with oil structuring techniques, aiming at the development of oleogels that show distinct lipid hydrolysis (lipolysis) rates, which could induce increasing bioacessibility levels of lipid soluble molecules.

A large number of reports have used diverse available lipid-based systems focusing on bioactive delivery, being most of them based on emulsion-template approaches. However, the potential to use edible oleogels or oil-structuring based systems towards delivery of bioactives, remain mostly unexplored. For example, curcumin, a natural bioactive and major bioactive of turmeric, is an interesting compound that has been associated to numerous health-promoting features like anti-diabetic, anti-cancer, anti-inflammatory, and antioxidant activities [42]. The major problem resides in its poor water solubility properties (as any other lipophilic molecule), thus hampering its delivery during digestion. This limitation in terms of absorption leads to restricted bioavailability levels ranging from 10 to 30% [43]. A study on the incorporation of curcumin oleogel (using glyceryl monostearate as MCT oil gelator) reported rapid digestion and elevated levels of bioaccessibility of curcuminoids [44]. In the sequence of that conclusion, Yu and Huang (2012), demonstrated that the development of a curcumin oleogel-based nanoemulsion conveyed even higher bioacessibility and a faster rate and extent of lipolysis, with *in-vitro* bioacessibility levels up to 47% [45]. This shows the ability of oleogels to increase the delivery of poorly soluble nutraceuticals in functional food products.

Ashkar *et al.*, recently reported how ethylcellulose, monoglycerides and di-glyceride, and a mixture of β-sitosterol + γ-oryzanol affected the digestive response of oleogels [46••]. This work using canola oil oleogels studied the impact on lipolysis of three types of gelators, showing the influence of the gelator network on the modulation of the digestive behaviour of oleogel structures targeting bioactivity. Differences among digestibility were a consequence of the nature of the gelator, structural effect of molecular weight, concentration of gelators and physical state. The increase of the gelators' molecular weight and gel hardness led to a lower extent of lipid breakdown. When compared to the control (unstructured oil), monoglycerides and di-glyceride based oleogels showed a higher degree of free fatty acids (FFAs) release (78–91%). In contrast, β-sitosterol + γ-oryzanol originated a lower lipolysis extent that did not exceed 39%.

A similar behaviour was observed by Andrade *et al.*, with digestion studies using loaded-complex emulsions with gelled interfaces, since the degree of release of bioactive compounds and the digestion kinetics was affected by the physical properties of the emulsion phases [47]. *In-vitro* digestion of capsaicin-loaded oleogels using medium chain triacylglycerol (MCT) showed an improved capsaicin bioaccessibility when incorporated in oil medium (regardless of MCT being presented as a liquid oil or an oleogel). Similar bioaccessibility levels (approx. 63%) were observed for capsaicin-loaded organogel and capsaicin-loaded MCT oil, being 10 times higher than those of free capsaicin [48].

The capability to control or delay the rate of carotenoids' release in the gut is very significant. The micellization rate of β-carotene and its consequent bioavailability will be dependent on the carrier structure [49]. The micellization rate of the bioactive incorporated in canola oil gelled with 12-hydroxystearic acid differed from the values exhibited by liquid canola oil with β-carotene during *in vitro* digestion. This study allowed to infer that the micellization rate was only affected by the physical network and there was no indication of any significant chemical effect on the lipid hydrolysis. A similar behaviour was found by Guo *et al.*, as protein emulsions stabilized by the gelation of rice bran wax showed a delay in terms of fatty acids release as a consequence of the rice bran crystallization effect on the structural disintegration and the formation of micelles [39]. This is consequence of the non-digestible tri-dimensional network that is strong enough to entrap the oil at a certain level. However, the increase of gelator concentration in the oleogels did not necessarily lead to lower lipolysis; instead, the increased amount of crystalline structures was responsible for oil droplet coalescence by means of crystal growth, that penetrated the oil-water interface, interacting with each other. At this stage, the imbalance in the oil-water interface was responsible for an extended lipid exposure to lipolysis, thus showing a higher free fatty acids release. Thus, an optimal balance in the composition of the system (i.e. oleogelator concentration), considering both droplet interface rigidity and kinetic stability of emulsion, is determinant to tailor the rate of lipolysis.

The significant impact exerted on the levels of postprandial plasma triglycerides, glycemia, and appetite has been reported by some *in vivo* studies [50]. Results of total cholesterol, adipose tissue accumulation and triacylglycerol levels allowed to conclude that rice bran oleogels' gel structure played a crucial role in decreasing the lipid digestibility in high-fat diets containing 30% of fat content [50]. In comparison to regular margarine ingestion, the introduction of the oleogel in the diet decreased about 30% of triacylglycerol levels in serum and liver and increased about 30% the amount of excreted triacylglycerol in the feces.

Outlook

Facing the number of strategies and potential combinations that can be applied in the field of oil structuring, there is still a lot of effort to be done to bridge the gaps between empirical and rational design of both multicomponent and oleogel-derived structures. The bottleneck is a better understanding on how oleogels' structures behave facing digestion conditions. Disclosing whether the structure itself or the ingredients are more relevant through this process is a noble rationale for upcoming researches. It seems fundamental for future food design, to enhance the scientific knowledge on oleogels' digestion performance as they function to deliver bioactive compounds. Tailoring digestion properties of oleogel-based structures and thus directly affecting the functional conditions of nutrients at the different stages of the gastro-intestinal digestive process is certainly an important advance towards customized nutrition and consumer wellbeing.

Conflict of interest statement

Nothing declared.

Acknowledgements

Paula Kiyomi Okuro thanks FAPESP (grant #2018/20308-3 São Paulo Research Foundation -FAPESP). Rosiane Lopes Cunha thanks CNPq-Brazil (307168/2016-6) for the productivity grant.

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