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Organogelation: it's food application

Abstract

There is growing evidence that dietary fat may linked to risk of a number of chronic disorders, such as coronary heart disease or type 2diabetes. Due to increasing consumer awareness to healthy and risk of saturated fat, food manufacturers are switching on novel technologies. One of novel technology is organogelation/oleogelation i.e. structuring of edible oils. The unique physical, functional, and nutritional properties of edible oil organogels has caught the eye of the food and pharmaceutical industries. These organogels are formed upon self assembly of surfactant-like small molecules into crystalline fibers at very low concentrations (wt 2%), which could be exploited for a variety of purposes in food products, from the manufacture of spreads to the solubilization, stabilization and delivery of lipid-soluble nutraceuticals. The use of oleo gels in the food industry is still in its infancy, but the potential is significant. This paper reviews about the traditional and current strategies of structuring oleo gels, types of gelators used in structuring and food applications.

Keywords: food, gelator, novel, nutraceutical, oleogel, organogel, pharmaceutical

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Abbreviations: TAG, tri acyl glycerol; DAG, di acyl glycerol; MAG, mono acyl glycerol; EC, ethyl cellulose

Introduction

Gels with the ability to immobilize a liquid phase are structures of three-dimensional network. These types of gels consist of two parts, gelling agent (network forming) and liquid solvent phase (hydrophilic or hydrophobic). However, depending on the polarity of the liquid immobilized within the networked structure, gels may be termed either as hydro gels (polar solvent-water) or organogels (organic solvent).[1] An organ gel can be defined as an organic liquid entrapped within a thermo-reversible, anhydrous and structured viscous-elastic material by a three-dimensional gel network, also referred to as oleo gels if the organic phase is edible oil. This simply means transformation of a liquid oil into a 'gel-like' structure with viscous-elastic properties This gel network is formed by the self-assembly of a relatively low concentration of low molecular weight compounds organogelator molecules; which are capable of gelling organic solvents.[2,3]

The replacement of solid fat in food products (fat mimetic) is the potential of oleo gels and the improvement in the nutritional profile of foods. Oleo gels can also be used in a variety of applications such as in cosmetics (to prevent oil leakage), pharmaceutical and biotechnology (for the encapsulation and/or controlled release of hydrophobic bioactive molecules). It can also be used to entrap organic solvents in plastic and paint industries.[4] The use of oleo gels in the food industry is just beginnings, but the potential is substantial.[2,5,6]

Structuring of oleo gels and current strategies

According to fundamental research perspective, organogelation with many characteristics is an interesting topic as it brings up important questions in basic research of study such as crystallization, surface chemistry/physics and materials science. One of these characteristics is that most organogels are relatively low-molecular weight compounds.[7–9] Organogel formations use those types of compounds which have ability to form a network. The ability of these compounds to gel a solvent is believed to be a balance between the solubility and insolubility of the gelator within the solvent. It should not to be either more soluble or insoluble. It should be relatively insoluble so that it can crystallize meso structures and soluble such that it can interact with solvent molecules.[9] Two structuring methods are used for oleo gel productions. These are traditional and non-traditional structuring methods. Currently non-traditional structuring method is frequently used.

Traditionally, oil structuring of TAG molecules is based on the molecular configurations and diversity of the molecules which permits the tailoring of physical properties of the fat according to the desired functionality of food product by using the modified processing methods or by changing the chemistry of the material. The majority of fat products available to the consumer are structured by a colloidal network of crystalline TAG particles. TAG that contains cis or Trans fatty acids will face a decrease in solubility on cooling below its melting point at ambient temperature. It is considered that saturated fatty acids become dissolve in unsaturated TAG phase and this leads to the formation of solid nuclei of TAG which further grow into crystalline nanoparticles or spherulitic particles. Organization of these spherulitic particles into arbitrary flocs establishes noncovalent interactions between fat crystal networks, which provide physical functionality to the fat material. The quantity of crystalline matter is an important parameter for determining the characteristics of the lipid material.[7,9,10]

A nontraditional way to structure oil with reduced levels of Trans and saturated fatty acids is based on the use of structurants which have potential of replacement of the natural network of TAG structure in the native fat. Now, several strategies have been developed to structure oil using different structurants, also termed gelators (Figure 1). These structurants should have following characteristics such as: food grade, economical, versatile, and efficient as lipid and matching physical properties to be used in food applications. Through molecular self assembly of particle or fibril crystallization can potentially lead to the formation of three-dimensional gel network which mimic TAG crystallization (Figure 1A & 1B). Such mechanism can be found in waxes, monoglycerides and diacylglycerol, fatty acids and fatty alcohols. The use of high concentration of particle filler could also lead to the configuration of a colloidal network that leads to the formation of oleo gels (Figure 1C).[11] Additional way to structuring oil is Liquid crystalline mesophases (Figure 1D).[12] Recent studies have explored the use of macromolecules as a gelator for vegetable oils such as ethyl cellulose (EC) (Figure 1E).[6,13]

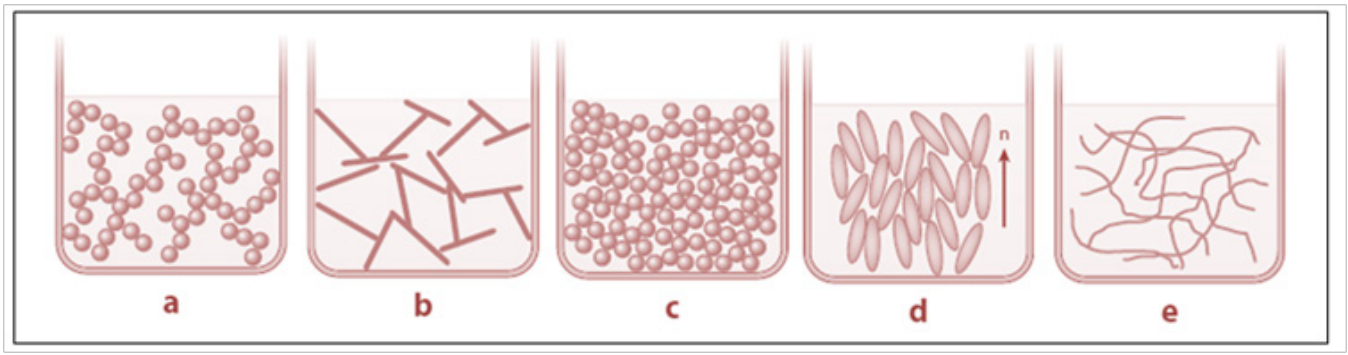

Figure 1 Schematic illustration of different strategies of oleo gel formation.

(A)Crystalline particle (B) Fibril network (C) Particle fillers (D) Liquid crystalline esophase (E) Polymer network

Types of organogelators

Oleogelators can be classified into two systems: crystal particle systems and self-assembly systems. In former the oleogelator involves crystal particles occurring through nucleation and subsequent growth of crystals in the oil phase, whereas in the latter involves a molecular-level self organization in the oil phases.[9,14] Another classification differentiates oleogelators between polymeric and low-molecular weight organogelators. Low-molecular weight organogels will be further categorized into two groups: lyotropic phases and crystalline dispersions. The main difference between the two is that lytropic phases include three parts (structuring, hydrophobic and hydrophilic solvent) whereas crystalline dispersion includes two parts (structuring and solvent). Examples of low molecular weight organogelators are TAG, DAG, MAG, fatty acids, fatty alcohols, waxes, wax esters and sorbitanmonostearate.[15] Polymeric organogelators show the promising ability in food sector as many are inexpensive and food grade compared with the former. Among them, ethyl cellulose shows particularly interesting potential.[5,9,16] Different strategies of structuring organogels using different types of gelators are summarized in Table 1.

Table 1 Different strategies, type of gelator and their examples

S. No	Type of strategy	Type of gelator	Example	References
1	Crystalline material	n-Alkanes	n-Tetracosane (C-24), n-octacosane (C-28), n-dotiacosane (C-32), and n-hexatriacosane (C-36)	29
		Carbamates	Carbamates with alkyl side chains of different lengths	30
		Waxes	Candelilla wax	31–34
			Rice bran wax	14,32
			Sunflower wax	32,35
			Carnauba wax	32
			Beewax	35,36
			Sugarcane	33
		Fatty acids and fatty alcohol	Stearic acid, stearyl alcohol	37–41
		Hydroxylated fatty acids	12-Hydroxystearic acid	17,34,42–45
		Monoacylglycerol (MAG)	Variety	46–48
		Diacylglycerol (DAG)	Dipaimitin and distearin	49
		Triacylglycerol (TAG)	High and low melting temperature TAG mixtures	50,51
		γ -Oryzanol/ phytosterol mixtures	Sterol ester γ - + phytosterol (dihydrocholesterol, cholesterol, β-sitosterol, cholestanol, stigmasterol)	52–55
		Ceramide	Sphingolipids	56,57
			Lecithin	58
			Lecithin+sorbitantristearate	3,59
			Lecithin and sitosterol	60
			Lecithin and α-tocopherol	61
			Sorbitanmonostereate (SMS)	62,63
			Sorbitanmonostereate (SMP)	64
			N-Lauroyl L-alanine and N-stearoyl L-alanine	65

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Table Continued

S. No	Type of strategy	Type of gelator	Example	References
2	Particle filler	Silica particles		20
3	Liquid Crystalline mesophase			12,66,67
4	Macromolecules	Polymer	Ethyl-cellulose (EC)	
			Isocyanate-functionalized methylcellulose (MC)	68
			Cellulose derivative mixtures (EC, MC and α-cellulose)	69,70
			Chitin, chitosan, and acylated derivatives	71
5	Other	Dried protein systems	B-Lactoglobulin	72,73
		Dried water soluble polysaccharide network	Hydroxypropyl methylcellulose (HPMC), methylcellulose (MC), xanthan gum	74,75
		Dried protein/ polysaccharide network	Gelatin and xanthan gum	76
		Shellac	NA	77,78

Food applications of oleo gels

Applied and basic research into the organogelation of hydrophobic solvents has skyrocketed in recent years. From an applied research perspective, organogels have a wide range of ''futuristic'' uses such as tissue engineering, template synthesis of inorganic nanostructures, biosensors and nanowires, to name a few. With regards to foods, cosmetics and pharmaceuticals, the applications in which there is the greatest interest relates the ability of organogels to structure non-polar solvents. In food sector, alteration of TAG structure is the main impetus which is provided by organ gel research.[9,17] The availability of alternative structurantsproduce food products with reduced content of saturated fatty acids and zero Tran's fatty acids. The various food applications of oleo gels are mentioned below or summarized in Table 2.

Table 2 Food applications of different types of gelators

S. No	Type of gelator	Food application	Reference
1	12-hydroxystearic acid	Reduced syneresis in peanut butter	79
		Prevent oil migration in cream-filled chocolate confection	2,4,21,22,80,81
		Controlled release of β-carotene	26
2	Ethyl cellulose	Prevent oil migration in cream fillings and cookies	5
		Reduction of saturated fat in frankfurters	16
	Ethyl cellulose (15%) or ethyl cellulose (11%) and sorbitan monostearate (3.67%)	All-beef frankfurters and pork breakfast sausages	82
3	Shellac	Prevent oil migration in chocolate paste	75
4	Sunflower wax and soya bean oil	Reduction of saturated fat in margarine	83,84
5	Rice bran wax	Reduction of saturated fat content in ice cream	85
6	Monoacylglycerols (0.5-2.5%), fatty alcohols (0.5-2.5%) or soy lecithin (2.5%)	Meat suspensions	86,87
7	Lecithin	Controlled release of nutraceuticals	19,88
8	Soy lecithin and palm oil oleo gel	Controlled release of nutraceuticals	89
9	Monostearin	Controlled release of curcuminoids	90.91
10	Carnauba wax and monoglyceride	Reduction of saturated fat in margarine	36

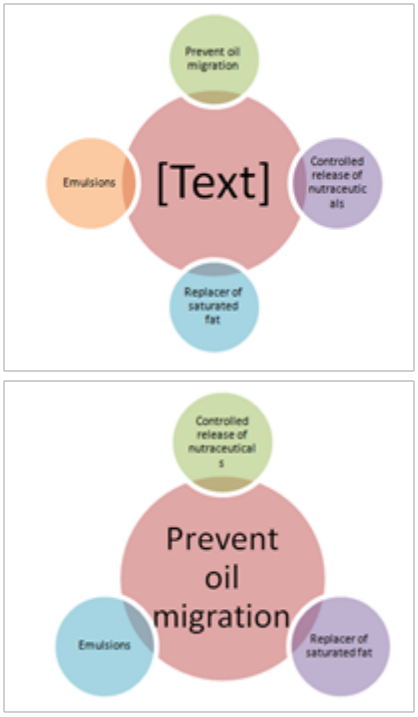

Figure 2 Different food applications of oleo gel.

Prevent of oil migration

The migration of oil is the movement of oil from liquid phase in a food, cosmetics and pharmaceutical preparation. The oil migration results in quality defects such as in chocolate confections, oil migration results in fat bloom.[18] For this reason, lipid scientists are constantly searching for new methods to control oil migration.[19,20] A potential strategy for preventing oil migration through confections is the gelation of any free oil which would be prone to migrate.[21,22] The structuring ability of organogels, make them used as oil migration inhibitors in food products,[21,22] studied 12-HSA organ gel is composed primarily of canola oil(w98% w/w), making its lipid profile highly unsaturated; with approximately 59% mono- and 30% poly- unsaturated fatty acids. The solid-like physical properties of the 12-HSA-canola oil organ gel allow it to be used as a spread; while the network prevents the oil from leaking into the food product to which it is applied. There are various studies related to use of organogelators as controller of oil separation in confectionary food products as reviewed in Table 2.

Controlled release of nutraceuticals

Controlled release technology is now widely used in the pharmaceutical industries, where drugs are either encapsulated by materials or incorporated into tablets that are designed specifically to delay or control the rate of drug release into the bloodstream after oral administration.[23] Since many important bioactive compounds are hydrophobic, it has been proposed that organogels be used to increase the solubility and control the release of non-polar pharmaceuticals and nutraceuticals.[21,22,24,25] Studies related to use of organogelators in nutraceuticals/pharmaceuticals are depicted in Table 2. One of the study stated by Turner et al.[25] that canola oil deliver/release β-carotene in between 0-30min during intestinal digestion while gel based oil have release duration of about 30-75min. So, the results proved that the bioactive compounds release kinetics and micellarization depend upon the physical matrix of lipid components.

Replacer of saturated fat

Many food manufactures are switching on other methods of replacement of saturated fat in food products as to cut the risk of cardiovascular diseases due to intake of Tran's fatty acids. Various studies are listed in Table 2 which summarized that organogelation is today's novel alternative method which provides different application in bakery, frying and confectionary products with low or zero Tran's fatty acids. In addition, based on the results described above, it was hypothesized that the gel network might also control the release of the lipids during digestion and therefore incites a more gradual or steady physiological response. For ex. Ethyl-cellulose (EC) is a new organogelator that is suitable for structuring vegetable oils. The glass transition temperature of EC is about 140°C and at this temperature EC dissolves completely and forms gel upon cooling. Therefore, EC is a good choice for replacing the saturated fats in different foods such as beef frankfurters.[26]

Emulsions

Due to the amphiphillic nature of some low molecular weight organogelator molecules, it has been proposed that they may be able to simultaneously stabilize and impart structure to water-in-oil emulsions. In other words, it may be possible to immobilize water droplets within a continuous gelled oil phase. With the proper formulation and processing conditions, organ gelled emulsions may have application as low-fat spreads or to control the release of both hydrophilic and hydrophobic bioactive compounds. This is a relatively new concept and accordingly, there is very little scientific literature published on this topic.[2,27,28]

Conclusion

Based on the evidence described in this review, it is clear that edible oil organ gel-based delivery systems are relatively new in food and these are three-dimensional networked structures with the ability to immobilize a liquid phase. Organogels can be formed by traditional and non-traditional methods but nowadays these are formed by non-traditional structuring technologies. It is summarized that various types of gelators are used during its formation such as fatty acids, alcohols, organic acids, waxes etc. It demonstrates significant futuristic promise and potential for a wide variety of applications in both food and pharmaceutical industries. However, much more work will be required to develop this technology into marketable consumer products.

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Conflict of interest

The author declares no conflict of interest.

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