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Mini-Review Article

Oleogels – types, properties and their food, and other applications

Stepan Akterian[1]✉, Eliza Akterian[2]

[1] *Division of Technology of edible, essential oils, perfumery and cosmetics. Technological Faculty. University of Food Technologies. Plovdiv, Bulgaria*
[2] *Faculty of Medicine. Medical University of Plovdiv, Plovdiv, Bulgaria*

Abstract

This review aims to reveal a modality for transforming liquid vegetable oils into semi-solid forms as their mechanical properties can vary from viscous and thick liquids to hard and elastic solids. The edible oleogels are an alternative replacer of undesirable trans and saturated fats. They are porous materials with self-assembled and three-dimensional gel network. Large amount of a continuous edible liquid-oil phase can be entrapped physically and stored in this gel structure. The bigels are a variety of oleogels and they represent two-phase emulsions, containing both oil-based oleogels and water-based hydrogels. The edible oleogels are composed by a structurant substance of food grade in a low concentration, below 10 %. Some of their featured properties are: (i) improved viscosity, spreadability and some of them are semisolid, translucent with semi-crystalline structure; (ii) high physical and structural stability combined with high oil binding capacity; (iii) high-temperature stability, but some of them are thermo-reversible; (iv) higher oxidative stability of oil and the chemical stability of active lipophilic compounds incorporated; (v) microbiological stability. Their more remarkable food applications are chocolates, processed meat products, margarine spreads and shortening. Their combination with other promising techniques raises up new perspectives for structural engineering of foods. There are also outlined other applications of oleogels in cosmetic and pharmaceutical formulations; for engineering purposes and environmental protection. The general limitations, some challenges in the development of new products, their commercialization are also divulged.

Keywords: gel, organogel, bigel, fat replacer, cosmetics, pharmaceutics, structural engineering

Abbreviations: EC – ethyl cellulose; DBS – 1,3:2,4-1,3:2,4-DibenzylideneD-sorbitol; GRAS – Generally Recognized As Safe by FDA; LMOGs – low-molecular-weight organogelators; TFAs – trans-fatty acids, WHO – World health organization; 12-HAS – 12-Hydroxyoctadecanoic acid

✉*Corresponding author: Prof. DSc Stepan Akterian, Division of Technology of edible, essential oils, perfumery and cosmetics, Technological Faculty, University of Food Technologies, 26 Maritza Blvd, 4000 Plovdiv, Bulgaria, tel.: +359 32 603 737, mobile: +359 889 902 806; E-mail:* dr.akterian@gmail.com

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Introduction

There is much proven evidence for negative metabolic effects of trans-fatty acids (TFAs) and the strong relationship between the coronary heart disease and the increased intake of TFAs (Mozaffarian et al. 2006, 2009; Nishida and Uauy 2009) and saturated fat (Nettleton et al. 2017). On this base of this evidence, the World Health Organization (WHO 2004) have recommended the consumption of trans and saturated fats to be reduced and shifted to monounsaturated or polyunsaturated fats and carbohydrates from whole grains. In addition to that, WHO dietary guidelines (WHO 2018a; Astrup et al. 2019) recommend strongly the intake of TFAs to be to less than 1% of total energy intake. The action package of WHO (2018b) have paved a roadmap towards the sustained elimination of industrial TFAs from the food supply. They recommend a preliminary limitation of these TFAs up to 2 g in 100 g of total oils and fats in all foods. Within existing food regulations, some countries like Canada and USA classified the fats industrially hydrogenated as unsafe. EU (2019) has introduced a mandatory regulation for limiting the contents of TFAs in the total fats up to 2 %. This regulation refers to the foods intended for the final consumer and it does not concern to TFAs naturally occurring in fat of animal origin.

There are various alternatives (Temkov and Mureşan 2021) for reducing TFAs like applying chemical and enzymatic esterification, using traditional fat replacers from lipid or non-lipid origin, employing oleogelation, applying genetic modification of the lipid in situ, using algae oil (Xue et al. 2020). However, each of the forenamed approaches has specific limitations. The traditional fat replacer represents a carbohydrate-, protein-, or lipid-based compound that replaces one or more of the functions of fats to reduce calories in foods (Chavan et al. 2016). Examples of lipid-based replacers are the low-calorie synthetic triglyceride caprenin (composed of caprylic C8:0, capric C10:0, and behenic C22:0 fatty acids), the synthetic triglyceride salatrim (composed of a random distribution of short-chain fatty acids C2:0, C3:0, C4:0 and long-chain fatty acids C18:0) and the non-caloric olestra (synthetic sucrose fatty acid polyester). The caprenin and salatrim simulate the properties of cocoa butter (Roller and Jones 1996). These fat replacers are widely commercialized. However, they have many limitations such as their applicability in low fat systems, they cannot expose at high temperature (as cooking, frying), they cannot meet all functional and sensorial requirements (Temkov and Mureşan 2021).

The gel stricture of oleogels is analogous to this of hydrogel. The latter was introduced by Bemmelen (1896). Hydrogels can absorb and store large amounts of water in their volume. These gels are mainly polymeric products in which cross-linked polymer chains form a three-dimensional network structure (Pal and Banerjee 2018). Nowadays, the hydrogels are employed widely in various food, pharmaceutical, cosmetic and other applications.

This review aims to present the oleogels as a modality for transforming liquid vegetable oils into alternative fat replacers (in semi-solid forms at room temperature), their types and specific properties. The second goal is the potential applications of oleogels in food formulations and in other non-food products to be outlined.

Oleogels, their types and specific properties

The first attempts for convenient applications of organogels in drug delivery started in the last years of the 20th century. The organogels consist of a solid three-dimensional, cross-linked gel network that spans a non-polar liquid organic phase such as vegetable and mineral oils including medium-chain triglyceride oil as well, ethyl oleate and ethylhexylphosphonic acid. There is current interest in their application in pharmaceutical, cosmetic, food and petrochemical industries. To distinguish the gels including vegetable oils from the traditional “organogels”, applied in chemical engineering, these edible-oil gels have been named oleogels (Marangoni and Garti 2011).

Heretofore, the Scopus database have registered 3615 documents with keywords oleogel or organogel. They comprise 3214 research articles, 180 reviews, 66 books and their chapters. Their growth trend is stable. (Fig. 1). The documents registered in the subarea of Agricultural and biological science are 527, including 438 research articles, 56 reviews and – 56 book chapters. If these documents in the food area were 18 for the first decade of the present century, their number in the second decade reached to 394 or the growth is more than 20 times. The breakdown by countries is as follows: China with 111 articles published, Canada - 69, USA - 65, Brazil - 39, Italy - 35, Spain - 34, Mexico - 31, Belgium - 25, Iran - 23, Portugal - 23, etc.

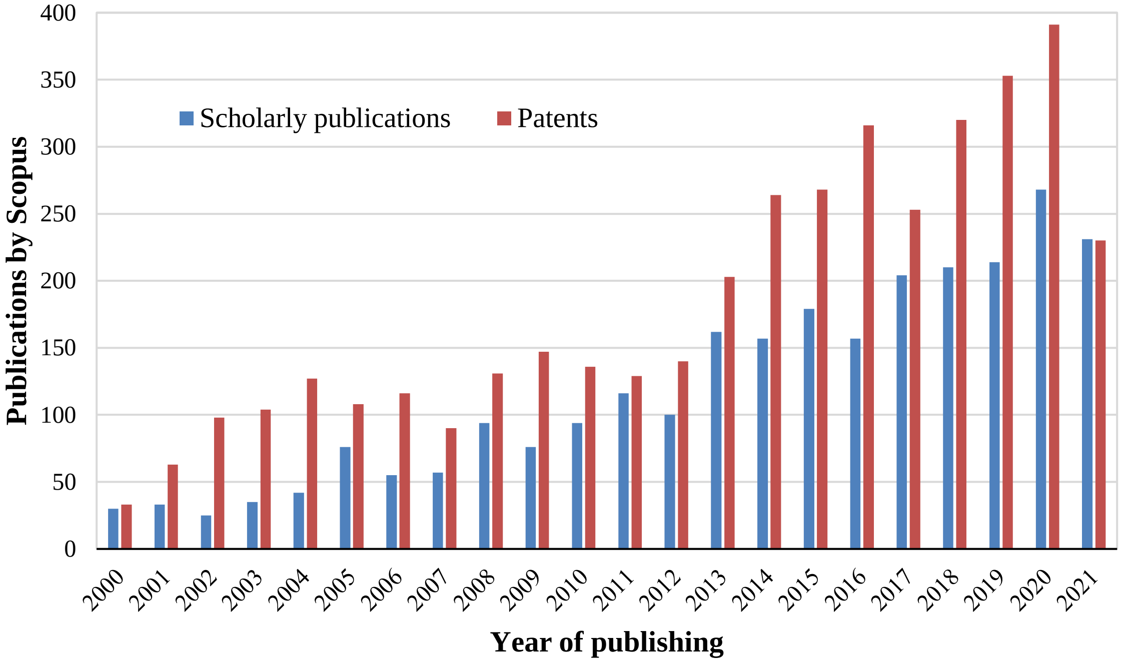

Figure 1. Evolution of the number of publications (scholarly articles and books, and patents) in the 21stcentury, registered in the Scopus database including the keywords oleogel or organigel

The **edible oleogels** are semisolid gel systems including a continuous edible liquid phase (like vegetable oil) that is entrapped physically in a self-assembled, three-dimensional, gel network composed by a structurant substance (organogelator in a low concentration, below 10 %) of food grade (Martins et al. 2018; Siraj et al. 2015). Some of these gels are thermo-reversible. The featured publication for these oleogels is the review of Co and Marangoni (2012).

The **bigels** represent two-phase emulsions, containing both oil-based oleogels and water-based hydrogels (Singh et al. 2018). Their investigation started in the second decade of the 21th century. Their general advantages are (Shakeel et al. 2019): the ability to deliver both hydrophilic and hydro-phobic components. The bigels draw attention for cosmetic, pharmaceutical and food applications as the interest to oleogel-in-hydrogel type of bigel is higher. A bi-continuous type with matrix-in-matrix arrangement was firstly reported by Lupi et al. (2016).

Three general routes were developed for liquid-oil structuring by employing different structurants (gelators). For the first route a gel network of crystalline particles is formed from low-molecular mass gelators like wax esters, fatty acids, fatty alcohols and monoglycerides. Fibrillar network structures are employed for the second route. A representative structurant for this route is the combination of sitosterol and oryzanol. The third route uses self-assembled gel structure from cross-linked polymer chains of macromolecules. A typical structurant is ethyl cellulose (Davidovich-Pinhas et al. 2016; Flöter et al. 2021).

The most promising **food grade structurants** are ethyl cellulose, natural waxes, phytosterols & orzanol, fatty acid derivatives and lecithin.

Ethyl cellulose (EC). It is a semisynthetic polysaccharide derived from cellulose as some hydroxyl end groups are replaced with more hydrophobic ethyl groups. It has been introduced in the early 1990s and extensively explored since then. For inducing the gelation process high temperatures (up to 150 ºC) should be applied. The EC oleogels have semi-crystalline structure. For that reason, the obtained oleogels remain stable at high temperatures. However, the rate of oil oxidation at these conditions also increases (Gravelle et al. 2018).

Natural waxes (of plant and animal origin) have food grade status and low cost. Candellilla wax, Carnauba wax, Rice Bran wax, Beeswax, Sunflower wax and plant shellac wax/resin represent the biggest interest for food applications. The concentration of sunflower wax for oil structuring is in the range of 0.5–10 % (Blake et al. 2018). The melting point of natural waxes is commonly between 50-80°C (Scharfe and Flöter 2020).

Phytosterols and oryzanol. The mixtures of plant sterol β-sitosterol and plant sterol ester γ-oryzanol form helical ribbon nanotubules. So, they self-assemble in a fine fibrillar network. The structured oleogels are firm, resembling a fat block, stable and translucent. These two phytosterol compounds occur as minor components in various vegetable oils. Both compounds foster for decreasing cholesterol absorption. γ-Oryzanol also acts as a natural antioxidant. A typical concentration of these structurants is about 10 %, in a proportion 40 % sitosterol and 60% oryzanol (Bot and Floter 2018).

Fatty acid derivatives like monoglycerides and sorbitan monostearate. Higher amounts of monoglycerides in oleogels result in higher gelation temperature and a higher density network. Some of these crystals can form a rosette-like shape. Sorbitan monostearate is responsible for forming opaque thermoreversible gels as the critical gelation concentration is about 10% (Chen and Terentjev 2018).

Lecithin in a combination of sorbitan tristearate or glyceryl monostearate can promote the formation of crystals, with a length of 10 µm, and stable oleogels.

Biodegradable low-molecular-weight gelators (up to 2 kDa). Renewable plant resources as noncalorific open-chain sugars are used in this green approach. Enzymes as lipases and proteases can be employed as biocatalysts in GRAS organic solvents for achieving an oleogelation via some self-assembly of low-molecular-weight gelators. A typical example is the regioselective acylation of carbohydrates by biocatalyst in vegetable oils for obtaining sugar-derived fatty acyl esters (Samateh et al 2011, 2020).

Applications

The number of patents issued is an indicator for the commercial interest to each new product. According to the Scopus database there are 5587 published patents related to oleogels or organogels. The trend of their growing is stable (Fig. 1). If their number in the last decade of the 20the century was 191, the patents for the first decade of the present century grew to 1153 and they reached to 2867 for the second decade. The breakdown of these patents by the territorial patent offices is as follows: United States - 3709, Japan - 823, Europe - 610, World WIPO - 479, United Kingdom - 99, etc.

The general areas of oleogels' application (Table 1) are in food, cosmetic, pharmaceutical formulations, in chemical engineering, environmental protection and their combining with other promising techniques.

Applications in the Food Systems. The existing applications of oleogels are mainly related to chocolate, dough & pastry, spreads, processed meat products, ice cream, margarine spreads, and shortening. Their general intention is a partial replacement of undesired trans and saturated fats in food systems with oleogels – structured unsaturated edible oils. Their properties like higher thermal resistance, desirable texture, structural stability, high physical and oxidative stability, and high oil binding capacity are very attractive for the potential food applications (Park and Maleky 2020).

Some challenges of ***chocolate*** manufacturing are higher thermal stability and less undesirable oil migration during storage. Adding EC dissolved in ethanol as a structurant polymer binding the fat phase can increase the thermal stability of chocolate. The added lecithin adsorbs onto the surface of sucrose crystals thereby it prevents the undesirable interactions between EC and sucrose. Mars Co. patented some applications of EC oleogels for heat-resistant chocolate (Stortz and Marangoni 2011). David et al. (2021) demonstrated the applicability of mercerized cellulose fiber powder as a structurant for oleogelating without any prior thermal treatment. The best results were obtained when bamboo fibers shorter than 120 µm had been employed. Finally, a dispersion of 30 % cellulose fibers in rapeseed oil was proffered for preparing a chocolate spread in place of saturated palm oil. The proposed formulation has a high thermal stability at 38°C, longer shelf life, very low oil clearance index after storage at 38°C for three weeks and on the other hand healthier nutritional quality due to the lower content of saturated fat and the higher content of unsaturated fat, and plant fibers.

Pastry products and cookies. Wax oleogels have been used for (i) partial fat replacement, (ii) preventing the gluten stands, (iii) obtaining the desired characteristics such as smoothness and uniform shape, gas-incorporation, moisture barrier, shelf life and tender mouthfeel. These oleogels have been prepared with virgin olive oil, flaxseed oil and soybean oil, structured using different types of waxes (like rice bran wax, sunflower wax, beeswax, candelilla wax) (Hwang et al. 2016). Oleogels with refined canola oil and ethylcellulose as structurant have been used in laminated pastries composed of many layers (Martins et al. 2018). For decreasing oil leakage during the storage of cookies, EC powder is added to the dough recipe. EC is dissolved in the oil phase during baking (usually at 175°C). After cooling, EC transforms the oil phase into oleogel (Stortz et al. 2012).

Table 1. Principle applications of oleogels and organogels

General areas of application	***Particular examples***
Food formulations	• heat-resistant chocolate (Stortz and Marangoni 2011; Patel et al, 2014; David et al. 2021) • pastry products and cookies with partial fat replacement (Stortz et al. 2012; Patel et al, 2014; Hwang et al. 2016; Martins et al. 2018) • low-fat ice cream (Zulim Botega et al. 2013; Moriano and Alamprese 2017; Silva-Avellaneda et al. 2021) • processed meat products with partial fat replacement (Barbut et al. 2016; Panagiotopoulou et al. 2016) • margarine spreads and shortening (Patel et al, 2014; Lopez-Martínez et al. 2015; Gravelle et al. 2017)
Cosmetic formulations	• topical and dermal applications (Almeida et al 2008; Balasubramanian et al. 2012; Shakeel et al. 2019; Lupi et al. 2013) • lipsticks (Heldermann 2016; Esposito and Kirilov 2021)
Pharmaceutical formulations	• topical and dermal applications (Prausnitz et al. 2004; Kumar and Katare 2005; Shaikh et al 2009; Balasubramanian et al. 2012) • oral applications of lipophilic active components (Masotta et al. 2019) • ophthalmic drugs (Hasda et al. 2020; Macoon and Chauhan 2021)
Chemical engineering	• lubricating greases (Sanchez et al. 2011a, 2011b, 2011c, 2011d) • solidifying flammable liquid organic solvents (Abdallah and Weiss 2000)
Environmental protection	• removing heavy-metals from aqueous solutions (Niia et al. 2010) • absorbing petrol oil spills (Bhattacharya et al. 2001)
Combining with other promising techniques	• oleogel-in-water Pickering emulsions (Qi et al. 2021) • extrusion 3D printing (Cotabarrena et al. 2019)

For manufacturing low-fat ***ice cream***, the milk cream was substituted by sunflower-oil based oleogels with a structurant based on phytosterols and γ-oryzanol (Moriano and Alamprese 2017) or rice bran wax oleogels combined with glycerol monooleate (Zulim Botega et al. 2013). Silva- Avellaneda et al. (2021) developed a new technology for making low-fat ice cream as this product consists of 46% whey protein and 7 % high oleic palm oil. For microfluidization this fluid mixture is forced through microchannels at high pressure of 121 MPa in order to the whey proteins to be fragmented into smaller particles. The latter increase the hydrophobic nature of these proteins that promotes self-assembling in a gel structure and obtaining stable oleogel. However, these technologies still remains in a laboratory stage.

Processed meat products like sausages and frankfurters. A particular substitution of pork fat has been done by incorporating different types of oleogels: (i) canola oil combined with ethyl cellulose (Barbut et al. 2016) and (ii) sunflower-oil oleogels employing γ-oryzanol and phytosterols as structurant (Panagiotopoulou et al. 2016). The latter can also contain rosemary oleoresin in the oil phase acting as antioxidant. The results show that the sausages with incorporated oleogels have similar texture, mouthfeel, juiciness, appearance, but not similar sensory perception by panelists.

Oleogel formulations can act as ***margarine spreads and shortening.*** There are reported wax formulations, EC oleogel combined with stearyl alcohol-stearic acid molecules or with monoacylglycerol for improving viscoelastic properties and stability (Gravelle et al. 2017; Lopez-Martínez et al. 2015). Oleogels based on shellac wax have been used for preparing low-fat spreads with desired consistency and mouthfeel (Patel et al. 2014).

Bhattacharya et al. (2001) demonstrated the usage of organogelators for the transformation of used edible oils wasted from kitchens with a view to their easy disposal and waste management.

Cosmetic Applications. The general advantages of oleogels for cosmetic applications are higher physical stableness of their formulations and chemical stability of active molecules, improved rheological properties, lower-cost composition and manufacturing preparation processes, the enhanced and versatile delivery of lipophilic compounds through skin (Martinez et al. 2019). Additional advantages of oleogels consisting mainly lipids are (i) the reduction of transepidermal water loss; (ii) improving water resistance of some products for lip care and sun protection for instance; (iii) a proper reduction of skin roughness for dry and cracked foot skin. Other their specific applications are used for decorative cosmetics like makeup, eye shadows, mascara; and for supportive care of diabetic skin, perianal skin disorders, and decubitus (Balasubramanian et al. 2012). Food grade structurants like lecithin, glyceryl fatty acid esters, sorbitan-derived esters, fatty acids, fatty alcohol, ethylcellulose and vegetable waxes have been wildly employed in cosmetic oleogels. Vegetable and some mineral oils are used in cosmetic olegels as the vegetable ones are preferred due to 'green' demands.

The oleogels based on plant waxes have been employed for formulating *lipsticks* (Heldermann 2016) whose basic ingredients are vegetable oil, pigments and waxes. The ration oil-to-wax should provide as (i) temperature stability and hardness even in summer or for the conditions of hot climate; (ii) smoothly spreading to lips; so too (iii) high oil-binding capacity for preventing unwanted surface oil bleeding at elevated temperature. The waxes of sunflower seeds and carnauba (obtained from the Brazilian palm *Copernicia prunifera*) represent the greatest interest for manufacturing lipsticks. The melting point of the first wax is approximately 78°C. Even at a low concentration of 2-3 %, this wax enables for obtaining high oil-binding capacity. It has no tendency to crystallize. For the lipsticks with this wax the plasticity and hardness of are well-balanced. They have long-lasting shine and glossiness. On another hand, the carnauba is the hardest natural wax used in cosmetics. Its melting point is approximately 84°C as its melting curve rises steeply. It provides a high degree of crystallization. For that, this wax allows to improve the temperature stability of lipsticks. However, this wax with high crystallinity reduces notably the glossiness of lipstick formulations. For a partial replacement of waxes in lipstick formulations Esposito and Kirilov (2021) employed low-molecular-weight organogelators (LMOGs): 12-Hydroxyoctadecanoic acid (12-HSA) and 1,3: 2,4 - 1,3: 2,4-DibenzylideneD-sorbitol (DBS) with molecular masses 300 and 358 Da, respectively. 12-HAS is derived from naturally occurring ricinoleic acid presents at 90 % in castor oil after the fractional distillation of this hydrolyzed hydrogenated oil. 12-HSA can form a self-assembled crystalline fibrillary network. The melting points are 82°C and 225°C, respectively for 12-HSA and DBS. These LMOGs entrap oil phase including a mixture of vegetable (as castor and almond oils) and mineral oils (as vaseline oil and white petrolatum). The gelling concentrations used are up to 1.5 and 10 %, respectively for DBS and 12-HSA. These researchers found that the sun protection factor of DBS-based lipsticks is significantly higher in a comparison with the traditional wax-based formulations; 12-HSA-based lipsticks are more heat stable; the firmness of lipsticks rises with the increase of LMOGs concentration. These authors concluded that LMOG-based formulations offer opportunities for fine-tuning the textural parameters of lipsticks.

The additional advantages of *bigels* are improved the permeability through the skin, moisturizing and cooling effects, better spreadability on the skin, better stability at room temperature, and good water washability (Shakeel et al. 2019). Almeida et al (2008) fist employed oleogel-in-hydrogel type of bigel for enhancing the moisturizing effect of cosmetic formulations. They revealed that this effect of bigels is higher than the effect of alone hydrogel. Another example of hydrogel-in-oleogel is the development of Lupi et al. (2013) that can be used as a cosmetic matrix for delivering both hydrophilic and lipophilic active molecules.

Other Applications. Oleoges and organogels have been also employed as a drug delivery system in transdermal, semisolid ***pharmaceutical formulations*** (Balasubramanian et al. 2012). Their advantages are (i) better viscosity, spreadability and higher physical stability; (ii) higher chemical stability of components; (iii) improved microbiological stability due to the lack of water in their formulations; (iv) better in vivo efficacy; (v) the simplicity in manufacturing. The oleogels are very convenient for topical applications. Lipids and oleogels respectively enhance the permeability of drug and reduce the side effects (Prausnitz et al. 2004). Kumar and Katare (2005) investigated the application of oleogel with a lecithin structurant for dermal formulations. Shaikh et al (2009) employed organogels based on lipophilic ethyl oleate as solvent and lecithin as a gelling agent for topical delivery of aceclofenac - nonsteroidal anti-inflammatory drug analog of diclofenac. They have found that the organogel formulation is more effective than the conventional hydrogels. There are also reported and other pharmaceutical applications as follow: Masotta et al. (2019) introduced an oleogel formulation for the oral application of lipophilic coenzyme Q_{10} in a high dosage drag. They employed oleogel with medium-chain triglyceride oil structured by ethyl cellulose and sorbitan monostearate. The active component in this formulation remains soluble and thermostable for 12 months of storage at room temperature. For delivering hydrophilic ophthalmic drugs to the eye, Macoon and Chauhan (2021) used oleogels based on soybean oil and structured by 10% ethyl cellulose as drug vehicle. They incorporated particles directly in the liquid oily phase of drag. For improving the corneal permeation of ocular drugs, Hasda et al. (2020) developed nano-composite oleogel based on organic cold-pressed virgin groundnut oil by using stearic acid as a structuring agent. For improving the cumulative permeation of the ocular drug delivery, graphene oxide in a concentration up to 0.05 % was added as filling agent. The corneal permeation of this oleogel formulation was investigated on the base of the employed antibacterial drug Ciprofloxacin HCl.

Lubricating greases are one of ***engineering*** applications of oleogels. Their advantages are higher thermal, mechanical and chemical stability, biodegradability and environmentally friendly. Oleogels based on chitin & chitosan, ethyl cellulose and other cellulose derivatives, sorbitan and glyceryl monostearates have been employed as structurantes for entrapping vegetable oils such as rapeseed, soybean and castor oil (Sanchez et al. 2011a, 2011b, 2011c, 2011d). Abdallah and Weiss (2000) applied the oleogel approach for the gelation of flammable liquid organic solvents.

Applications for environmental protection. Niia et al. (2010) employed organogels using dodecyl acrylate and divinyl benzene as gelators for entrapping di-2-ethylhexyl phosphoric acid or ethylhexyl-phosphonic acid. They demonstrated the possibility of these organogels to act as metal extractants for absorbing metal ions (Zn and Cu) from their hydrochloric acid solutions. After five cycles of sorption/ desorption the performance of the extractant was retained more than 98%. Their results show the potential of organogel with relevant extractant to remove heavy-metal ions from their aqueous solutions. Organogelators can be also employed for the treatment of petrol oil spills and for absorbing the oil (Bhattacharya et al. 2001).

The combination of oleogelation with other promising techniques can reveal new perspectives for structural engineering of foods. The first example is related to oleogel-in-water Pickering emulsions stabilized by cellulose nanocrystals (Qi et al. 2021). The researchers employed beeswax oleogel structured soybean oil. Such emulsions could be used as delivery systems for nutrients, bioactive and flavor compounds, or semisolid ingredients for reduced fat foods. Extrusion 3D printing using oleogels (Cotabarrena et al. 2019) is the second example. The employed oleogel consisted of a structurant mixture of monoglycerides and phytosterols for structuring high oleic sunflower oil. The extrusion-based 3D printer formed nutraceutical oral tablets with incorporated liposoluble active ingredients.

Conclusion and Future Perspectives

The oleogelation is powerful and flexible technique for structural engineering. The oleogels based on vegetable and marine oils act as an alternative replacer of trans- and saturated fats in food products. It has been displayed that a large amount of food-grade compounds in small concentrations are capable to promote oil gelation as structurants. The oleogels have been incorporated in various food systems. They can be a flexible tool for developing new tailored foods. The latter could meet the requirements of consumers with special needs (e.g. elderly people) and specific nutritional requirements (e.g. the delivery of proteins, microelements and some biologically active components).

However, there are many challenges for elaborating successful commercial applications and for scaling-up from a laboratory bench to industrial technology. For that, the further studies should reveal a clearer understanding of the involved metabolic processes and the overall impact of oleogels on human digestion (Park and Maleky 2020). Additional research on the physical behavior and chemical stability of oleogels should be completed depending on the presence of other ingredients in food systems. Nowadays, the price of structured oils is not competitive in a comparison of palm oil (500 USD per t). In economic aspect, the structured oils using waxes (such as sunflower, rice bran and sugarcane waxes) and ethylcellulose as gelators would be more reasonable for further commercialization. The price of such types of structured oils was evaluated at around 901-915 USD per t. Taking also this into account, it is considered that the oileogels based on the waxes and ethylcellulose, are the most promising for application in food formulations (Scharfe and Flöter 2020). However, the main challenge of developing new foods with incorporated oleogels is their ability to mimic better the mouthfeel, the taste and the texture of commonly used fats. The consumer acceptance of food products including oleogels could be also increased by flavor, aroma and texture development of new food products. This acceptance should be evaluated by proper sensory panels. Finally, the consumer acceptance remains the most critical factor for further successful large-scale industrial manufacturing of food products with oleogels employed. Therefore, the present affords are mainly directed to a partial replacement of saturated fats in food formulations.

The present cosmetic and pharmaceutical applications demonstrate that the oleogels are a versatile form for enhanced delivering both hydrophilic and lipophilic biologically active compounds to skin and not only. Their additional advantages are higher chemical stability of active components, improved physical stability and viscosity of formulations, low-cost composition used and preparation processes employed. However, for the large-scale production of oleogel-based cosmetic formulations, there are still some challenges and limitations. Further studies on the long-term skin compatibility of oleogels, their efficacy and the lack of unacceptable toxicological effects should guarantee the safety of final products (Martinez et al. 2019).

There are also some general difficulties (Martinez et al. 2019) for predicting the successful gelation process due to the present of contaminations in ingredients and the unrefined control of process variables (e.g. temperature, pH); the swelling of oleogel formed as well. For further successful commercialization of oleogel applications, the methods for characterizing their structure and evaluating their functional properties should be extended and sophisticated as well (Flöter et al. 2021).

References

Abdallah D.J., Weiss R.G. Organogels and low molecular mass organic gelators. *Advvanced Materials*, 2000, 12(17): 1237-1247. https://doi.org/10.1002/1521-4095(200009)12:17<1237::AID-ADMA1237>3.0.CO;2-B

Almeida I.F., Fernandes A.R., Fernandes L., Pena Ferreira P.C., Costa P.C., Bahia M.F. Moisturizing effect of oleogel/hydrogel mixtures. *Pharmaceutical Development and Technology*, 2008, 13(6): 487-494. https://doi.org/10.1080/10837450802282447

Astrup A., Bertram H.C.S., Bonjour J.-P., de Groot L.C.P., Otto M.C.O., Feeney E.L., Garg M.L., Givens I., Kok F.J., Krauss R.M., Jordan D., Lamarche B., Lecerf J.-M., Legrand P., McKinley M., Micha R., Michalski M.-C., Mozaffarian D., Soedamah-Muthu S.S. WHO draft guidelines on dietary saturated and trans fatty acids: time for a new approach? *BMJ*, 2019, 366(7): l4137. https://doi.org/10.1136/bmj.l4137

Balasubramanian R., Damodar, G., Sughir, A. Oleogel: A promising base for transdermal formulations. *Asian Journal of Pharmaceutics*, 2012, 6(1): 1-9. https://doi.org/10.4103/0973-8398.100118

Barbut S., Wood J., Marangoni A. Quality effects of using organogels in breakfast sausage, *Meat Science*, 2016, 122(12): 84-89. https://doi.org/10.1016/j.meatsci.2016.07.022

Bemmelen J.M. Der Hydrogel und das kristallinische Hydrat des Kupferoxydes. *Néerl*. 1896, 30: 1-24 – Published: January 1907 in: *Zeitschrift für Chemie und Industrie der Kolloide*. 1907, 1(7): 213-214. https://doi.org/10.1007/BF01830147

Bhattacharya S. Krishnan-Ghosh Y. First report of phase selective gelation of oil from oil/water mixtures. Possible implications toward containing oil spills. *Chemical Communications*, 2001, 37(2): 185-186. https://doi.org/10.1039/B007848O

Blake A.I., Toro-Vazquez J.F., Hwang H.-S. Wax Oleogels. In: *Edible Oleogels* (A.G. Marangoni, N. Garti Eds.). Champaign, AOCS Press. 2018, pp. 133-171, ISBN: 978-0-12-814270-7, https://doi.org/10.1016/C2017-0-00541-4

Bot A., Floter E. Edible Oil Oleogels Based on Self-assembled β-Sitosterol and γ-Oryzanol Tubules. In: *Edible Oleogels* (A.G. Marangoni, N. Garti Eds.). Champaign, AOCS Press. 2018, pp. 31-63, ISBN: 978-0-12-814270-7, https://doi.org/10.1016/C2017-0-00541-4

Chavan R.S., Khedkar C.D., Bhatt S. Fat Replacer. In: *The Encyclopedia of Food and Health* (B. Caballero, P. Finglas, F. Toldrá Eds.). Academic Press. 2016, vol. 2, pp. 589-595. ISBN: 978-0-12-384953-3

Chen C.-H., Terentjev E.M. Monoglycerides in Oils. In: *Edible Oleogels* (A.G. Marangoni, N. Garti Eds.). Champaign, AOCS Press. 2018, pp. 103-131, ISBN: 978-0-12-814270-7, https://doi.org/10.1016/C2017-0-00541-4

Co E.D., Marangoni A.G. Organogels: an alternative edible oil-structuring method. *JAOCS*, 2012, 89(5): 749-780. https://doi.org/10.1007/s11746-012-2049-3

Cotabarrena I.M., Crucesa S., Palla C.A. Extrusion 3D printing of nutraceutical oral dosage forms formulated with monoglycerides oleogels and phytosterols mixtures. *Food Research International*, 2019, 126(12): 108676. https://doi.org/10.1016/j.foodres.2019.108676

David A., David M., Lesniarek P., Corfias E., Pululu Y., Delample M., Snabre P. Oleogelation of rapeseed oil with cellulose fibers as an innovative strategy for palm oil substitution in chocolate spreads. *Journal of Food Engineering*, 2021, 292(3): 110315. https://doi.org/10.1016/j.jfoodeng.2020.110315

Davidovich-Pinhas M., Barbut S., Marangoni A.G. Development, Characterization, and Utilization of Food-Grade Polymer Oleogels. *Annual Review of Food Science and Technology*, 2016, 7(4): 65-97. https://doi.org/10.1146/annurev-food-041715-033225

Esposito C.L, Kirilov P. Preparation, Characterization and Evaluation of Organogel-Based Lipstick Formulations: Application in Cosmetics. *Gels*, 2021, 7(3): 97. https://doi.org/10.3390/gels7030097

European Commission Regulation (EU) 649 of 24 April 2019 as regards trans-fat, other than trans-fat naturally occurring in fat of animal origin. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32019R0649

Flöter E., Wettlaufer T., Conty V., Scharfe M. Oleogels - their applicability and methods of characterization. *Molecules*, 2021,; 26(6): 1673. https://doi.org/10.3390/molecules26061673

Gravelle A.J., Davidovich-Pinhas M., Barbut S., Marangoni A.G. Influencing the crystallization behavior of binary mixtures of stearyl alcohol and stearic acid (SO-SA) using ethylcellulose. *Food Research Inter*national, 2017, 91(1): 1-10. https://doi.org/10.1016/j.foodres.2016.11.024

Gravelle A.G., Marangoni A.G., Davidovich-Pinhas M. Ethylcellulose Oleogels. In: *Edible Oleogels* (A.G. Marangoni, N. Garti Eds.). Champaign, AOCS Press. 2018, pp. 331-362, ISBN: 978-0-12-814270-7, https://doi.org/10.1016/C2017-0-00541-4

Hasda A., Vuppaladadium S., Qureshi D., Prasad G., Mohanty B., Banerjee I., Shaikh H., Anis A., Sarkar P., Pal K. Graphene oxide reinforced nanocomposite oleogels improves corneal permeation of drugs. *Journal of Drug Delivery Science and Technology*, 2020, 60(12): 102024. https://doi.org/10.1016/j.jddst.2020.102024

Heldermann M. Get the Perfect Lipstick: Boost Oil-binding Capacity with Natural Waxes. *Cosmetics and Toiletrie*, 2016, 131(7): 23. https://www.cosmeticsandtoiletries.com/formulating/category/color/Get-the-Perfect-Lipstick-Boost-Oil-binding-Capacity-With-Natural-Waxes-394615431.html

Hwang H.S., Singh M., Lee S. Properties of cookies made with natural wax-vegetable oil organogels, *Journal of Food Sci*ence, 2016, 81(5): 1045–1054. https://doi.org/10.1111/1750-3841.13279

Kumar R., Katare O.P. Lecithin organogels as a potential phospholipidstructured system for topical drug delivery: A review. *AAPS Pharmscitech*, 2005, 6: E298-E310. https://doi.org/10.1208/pt060240

Lopez-Martínez A., Charo-Alonso M.A., Marangoni A.G., Toro-Vazquez J.F. Monoglyceride organogels developed in vegetable oil with and without ethylcellulose. *Food Research International*, 2015, 72(6): 37-46. https://doi.org/10.1016/j.foodres.2015.03.019

Lupi F.R., Gabriele D., Baldino N., Mijovic P., Parisic O.I., Puoc F. Olive oil/policosanol organogels for nutraceutical and drug delivery purposes. *Food & Function*, 2013, 4(10): 1512-1520. https://doi.org/10.1039/c3fo60259a

Lupi F.R., Shakeel A., Greco V., Oliviero R.C., Baldino N., Gabriele D. A rheological and microstructural characterisation of bigels for cosmetic and pharmaceutical uses. *Materials Science and Engineering: C*, 2016, 69(12): 358-365. https://doi.org/10.1016/j.msec.2016.06.098

Macoon R., Chauhan A. Ophthalmic delivery of hydrophilic drugs through drug-loaded oleogels. *European Journal of Pharmaceutical Sciences*, 2021, 158(3): 105634. https://doi.org/10.1016/j.ejps.2020.105634

Marangoni A.G., Garti N. Edible Oleogels. Structure and Health Implications. (First Edition). AOCS, Urbana, 2011, pp. ISBN: 978-0-9830791-1-8. https://doi.org/10.1016/C2015-0-02413-3

Martinez R.M., Rosado C., Velasco M.V.R., Lannes S.C.S., Baby A.R. Main features and applications of organogels in cosmetics. *International Journal of Cosmetic Science*, 2019, 41(2): 109-117. https://doi.org/10.1111/ics.12519

Martins A.J., Vicente A.A., Cunhab R.L., Cerqueira M.A. Edible oleogels: an opportunity for fat replacement in foods. *Food & Function*, 2018, 9(2): 758-773. https://doi.org/10.1039/c7fo01641g

Masotta N.E., Martinefski M.R., Lucangioli S., Rojas A.M., Tripodi V.P. High-dose coenzyme Q10-loaded oleogels for oral therapeutic supplementation. *International Journal of Pharmaceutics*, 2019, 556(2): 9-20. https://doi.org/10.1016/j.ijpharm.2018.12.003

Moriano M. E. and Alamprese C. Organogels as novel ingredients for low saturated fat ice creams, *LWT – Food Science and Technology*, 2017, 86(7): 371-376. https://doi.org/10.1016/j.lwt.2017.07.034

Mozaffarian D, Aro A., Willett WC. Health effects of trans-fatty acids: experimental and observational evidence. *European Journal of Clinical Nutrition*, 2009, 63(2): S5-S21. https://doi.org/10.1038/sj.ejcn.1602973

Mozaffarian D., Katan, M.B., Ascherio, A., Stampfer, M.J., Willett, W.C. Trans-fatty acids and cardiovascular disease. *The New England Journal of Medicine*, 2006, 354(4): 1601-1613. https://doi.org/10.1056/NEJMra054035

Nettleton J.A., Brouwer I.A., Geleijnse J.M., Hornstra G. Saturated fat consumption and risk of coronary heart disease and ischemic stroke: a science updated. *Annals of Nutrition and Metabolism*, 2017, 70(1): 26-33. https://doi.org/10.1159/000455681

Niia S., Okumuraa S., Kinoshitab T., Ishigakib Y., Nakanob K., Yamaguchib K., Akitab S. Extractant-impregnated organogel for capturing heavy metals from aqueous solutions. *Separation and Purification Technology*, 2010, 73(2): 250-255. https://doi.org/10.1016/j.seppur.2010.04.009

Nishida C., Uauy R. WHO Scientific update on health consequences of trans fatty acids: Introduction. *European Journal of Clinical Nutrition*, 2009, 63(2): S1-4. https://doi.org/10.1038/ejcn.2009.13

Pages Pal K., Banerjee I. *Polymeric Gels. Characterization, Properties and Biomedical Applications* (First Edition). Woodhead Publishing. 2018, pp. 231-249, ISBN: 978-0-08-102179-8, https://doi.org/10.1016/C2016-0-04092-5

Panagiotopoulou E., Moschakis T., Katsanidis E. Sunflower oil organogels and organogel-in-water emulsions (part II): Implementation in frankfurter sausages, *LWT – Food Science and Technol*ogy, 2016, 73(11): 351-356. https://doi.org/10.1016/j.lwt.2016.03.004

Park C., Maleky F. A critical review of the last 10 years of oleogels in food. Mini review. *Frontiers in Sustainable Food Systems*, 2020, 4(9): 00139. https://doi.org/10.3389/fsufs.2020.00139

Patel A.R., Rajarethinem P.S., Gredowska A., Turhan O., Lesaffer A., De Vos W.H., Van de Walle D., Dewettinck K. Edible applications of shellac oleogels: spreads, chocolate paste and cakes, *Food & Function*, 2014, 5(4): 645-652. https://doi.org/10.1039/C4FO00034J

Prausnitz M.R., Mitragotri S., Langer R. Current status and future potential of transdermal drug delivery. *Nature Reviews Drug Discovery*, 2004, 3(2): 115-124. https://doi.org/10.1038/nrd1304

Qi W., Li T., Zhang Z., Wu T. Preparation and characterization of oleogel-in-water swelling pickering emulsions stabilized by cellulose nanocrystals. *Food Hydrocolloids*, 2021, 110(1): 106206. https://doi.org/10.1016/j.foodhyd.2020.106206

Roller S., Jones S.A. *Handbook of Fat Replacers* (First Edition). CRC Press. 1996. 336 pages. Print ISBN: 9780849325120

Samateh M., Sagiri S., John G. Molecular Oleogels: Green Approach in Structuring Vegetable Oils. In: *Edible Oleogels* (A.G. Marangoni, N. Garti Eds). First Edition. AOCS. 2011, pp. 415-438, Print ISBN: 978-1-4665-8668-0, eBook ISBN: 978-0-3678-0206-6, https://doi.org/10.1016/B978-0-12-814270-7.00018-6

Samateh M., Sagiri S., Sanni R., Chee C., Satapathy S., John G. Tuning aesthetic and mechanical properties of oleogels via formulation of enzyme-enabled stereoisomeric molecular gelators. *Journal of Agricultural and Food Chemistry*, 2020, 68(46): 13282-13290. https://doi.org/10.1021/acs.jafc.0c00185

Sanchez R., Franco J.M., Delgado M.A., Valencia C., Gallegos C. Rheological and mechanical properties of oleogels based on castor oil and cellulosic derivatives potentially applicable as bio-lubricating greases: Influence of cellulosic derivatives concentration ratio. *Journal of Industrial and Engineering Chemistry*, 2011a, 17(4): 705-711. https://doi.org/10.1016/j.jiec.2011.05.019

Sanchez R., Franco J.M., Delgado M.A., Valencia C., Gallegos C. Rheology of oleogels based on sorbitan and glyceryl monostearates and vegetable oils for lubricating applications. *Grasas y Aceites*, 2011b, 62(3): 328-336. https://doi.org/10.3989/gya.113410

Sanchez R., Stringari G.B., Franco J.M., Valencia C., Gallegos C. Thermal and mechanical characterization of cellulosic derivatives-based oleogels potentially applicable as bio-lubricating greases: Influence of ethyl cellulose molecular weight. *Carbohydrate Polymers*, 2011c; 83(1): 151-158. https://doi.org/10.1016/j.carbpol.2010.07.033

Sanchez R., Stringari G.B., Franco J.M., Valencia C., Gallegos C. Use of chitin, chitosan and acylated derivatives as thickener agents of vegetable oils for biolubricant applications. *Carbohydrate Polymers*, 2011d; 85(3): 705-714. https://doi.org/10.1016/j.carbpol.2011.03.049

Scharfe M., Flöter E. Oleogelation: from scientific feasibility to applicability in food products. *European Journal of Lipid Science and Technology*, 2020, 122(12): 2000213. https://doi.org/10.1002/ejlt.202000213

Shaikh I.M., Jadhav S.L., Jadhav K.R., Kadam V.J., Pisal S.S. Aceclofenac organogels: In vitro and in vivo characterization. *Current Drug Delivery*, 2009, 6(1): 1-7. https://doi.org/10.2174/156720109787048320

Shakeel A., Farooq U., Iqbal T., Yasina S., Lupi F.R., Gabriele D. Key characteristics and modelling of bigels systems: A review. *Materials Science & Engineering* C, 2019, 97(4): 932-953. https://doi.org/10.1016/j.msec.2018.12.075

Silva-Avellaneda E., Bauer-Estrada K.R.E., Quintanilla-Carvajal X. The effect of composition, microfluidization and process parameters on formation of oleogels for ice cream applications. *Scientific Reports*, 2021, 11(3): 7161. https://doi.org/10.1038/s41598-021-86233-y

Singh V.K., Qureshi D., Nayak S.K., Pal K. Bigels. In: *Polymeric Gels* (K. Pal, I. Banerjee Eds). Elsevier. 2018, pp. 265-282, ISBN: 978-0-08-102179-8, https://doi.org/10.1016/b978-0-08-102179-8.00010-7

Siraj N., Shabbir M.A., Ahmad T., Sajjad A., Khan M.I., Butt M.S. Organogelators as a saturated fat replacer for structuring edible oils, *International Journal of Food Properties*, 2015, 18(9): 1973-1989. https://doi.org/10.1080/10942912.2014.951891

Stortz T.A., Marangoni A.G. Heat resistant chocolate. *Trends in Food Science & Technology*, 2011, 22(5): 201-214. https://doi.org/10.1016/j.tifs.2011.02.001

Stortz T.A., Zetzl A.K., Barbut S., Cattaruzza A., Marangoni A.G. Edible oleogels in food products to help maximize health benefits and improve nutritional profiles. *Lipid Technol*ogy, 2012, 24(7): 151-154. https://doi.org/10.1002/lite.201200205

Temkov M., Mureşan V. Tailoring the structure of lipids, oleogels and fat replacers by different approaches for solving the trans-fat issue - a review. *Foods*, 2021, 10(6); 1376. https://doi.org/10.3390/foods10061376

WHO. Draft Guidelines: Saturated fatty acid and trans-fatty acid intake for adults and children. 2018a. Geneva: WHO. Available at: https://extranet.who.int/dataform/upload/surveys/666752/files/Draft%20WHO%20SFA-TFA%20guidelines_04052018%20Public%20Consultation(1).pdf (accessed on 2 Aug 2021)

WHO. REPLACE trans-fat: an action package to eliminate industrially produced trans-fatty acids. WHO/NMH/NHD/18.4., 2018b. Available at: https://apps.who.int/iris/bitstream/handle/10665/331301/WHO-NMH-NHD-18.4-eng.pdf?squence=1&isAllowed=y

WHO. Global Strategy on Diet, Physical Activity and Health. Geneva, WHO, 2004. Available at: https://www.who.int/publictions/i/item/9241592222

Xue Z., Yu Y., Yu W., Gao X., Zhang Y., Kou X. Development prospect and preparation technology of edible oil from microalgae. *Frontiers in Marine Science*, 2020, 7(6): 00402. https://doi.org/10.3389/fmars.2020.00402

Zulim Botega D.C., Marangoni A.G., Smith A.K., Goff H.D. The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream, *Journal of Food Sci*ence, 2013, 78(9): 1334-1339. https://doi.org/10.1111/1750-3841.12175