Chapter 4
Oleogel Preparation Methods and Classification

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Abbreviations

12-HSA	12-hydroxystearic acid
CMCS	Carboxymethyl chitosan
DE	Degree of esterification
DG	Diglyceride
DSC	Differential scanning calorimetry
EC	Ethylcellulose
FD	Freeze drying
GRAS	Generally recognized as safe
HMWG	High molecular weight gelator

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HPMC	Hydroxypropyl methyl cellulose
HSP	Hansen solubility parameter
LMWG	Low molecular weight gelator
MC	Methylcellulose
MCT	Medium chain triacylglycerol
MG	Monoglyceride
SC-CO_2	Supercritical carbon dioxide
TAG	Triacylglyceride
USES	Ultrasound-enhanced electrospinning
WPI	Whey protein isolate

4.1 Introduction

Oleogels are edible, semi-solid, self-supporting, often anhydrous lipid-based materials. They belong to the class of fat mimetics and have been developed to substitute solid fats (at room temperature) such as palm oil, coconut oil, lard, tallow, butter, and margarine in food products, possibly without jeopardizing their structure, appearance, and sensory attributes [1, 2]. As described in Chaps. 2 and 3, excessive consumption of solid fats which contain saturated fatty acids has been associated with deleterious effects on human health, like cardiovascular diseases, diabetes type 2, cancer, and onset of obesity [3, 4]. To reduce the risk factors associated with saturated fats, their substitution with liquid oils containing unsaturated fatty acids is recommended. However, direct substitution in food products is not possible, as it can result in the loss of the structure provided by solid fats, which plays a vital role in food's sensorial attributes and physical appearance [1]. Oleogels can overcome this problem because their texture and appearance are tailorable and vary from an opaque spreadable lipid gel like margarine to an elastic or brittle translucent/transparent material like silicone or rubber, and usually, they contain more than 70% of edible liquid oils. Oil is converted to oleogels using structuring/gelling molecules called oleogelators (or organogelators). The term oleogel is typically used as a synonym for organogel, even though the latter term refers to any gel containing an organic solvent that can be either edible like vegetable, marine, and animal oils, or non-edible like acetone and hexadecane; oleogels contain only edible oils, being more appropriately considered a subclass of organogels.

Oleogels can be obtained using small molecules or (bio)polymers. In the first case, the oleogelators are called *low molecular weight gelators* (LMWGs), whereas in the second case, the term used is *high molecular weight gelators* (HMWGs). Examples of LMWGs are monoglycerides, fatty alcohols, fatty acids, waxes from plant and animal origin, plant sterols and their esters, and mixtures thereof [1]. On the other hand, proteins, polysaccharides, and their chemically derived counterparts, like cellulose, methylcellulose, ethylcellulose, xanthan gum, carrageenans, chitosan, chitin, and milk proteins are examples of HMWGs used to fabricate oleogels [1, 5]. A list of the most studied gelators can be found in Table 4.1 (Sect. 4.2).

To successfully obtain an oleogel, one needs to understand the physical form and physico-chemical properties of the gelators. For example, an important factor to consider is the balance between solubility and insolubility of the gelator in the solvent (oil, in this case). When there is balance, oleogels can be formed, whereas imbalances lead the gelator to precipitate or to fully solubilize, generating in both cases unstructured oils [60]. The majority of LMWGs and some HMWGs can be dissolved in oils at temperatures above their melting or glass transition temperature, and during cooling, they self-assemble forming a network that entraps the oil and gels the system [1]. We refer to this case as a *hot direct method*. However, even if the gelator is insoluble in oil, it can still be used for oleogel preparation. For example, the majority of HMWGs are insoluble in oil but soluble in water, ethanol, or aqueous solutions. Therefore, these gelators can be solubilized in molecular form or dispersed as aggregates. Usually, they are added in a solvent other than oil to fabricate structures used as templates, where oil is retained or absorbed to form an oleogel. In this pre-oleogel stage, we can find hydrogels, emulsions, foams, fibers, or encapsulated lipids. Hydrogels are usually converted into solvent-gels (by exchanging the water phase with an organic solvent, *via* a stepwise solvent substitution) or aerogels (using for example supercritical carbon dioxide drying) before being further converted into an oleogel [61, 62]. On the other hand, emulsions (with or without droplet crosslinking) and foams are dried before being converted into an oleogel [63, 64]. Fibers obtained through electrospinning are cut through wet milling/shearing before being converted into an aerogel and then to an oleogel, or directly used in oil to form oleogels [66–68]. Finally, encapsulated lipids are obtained by coating solid lipid droplets with biopolymers and then melted in oil to obtain during cooling an oleogel structured through a hybrid network composed of biopolymers and solid lipids [68]. Therefore, any methods where a second solvent (like water) is necessary to solubilize or disperse gelators, but it is removed before obtaining the final oleogel, are called *indirect methods*. Finally, there are some cases where gelators are insoluble both in oil and water and can be used as particles. If the particles can structure the oil by direct dispersion at, or below room temperature, we refer to this method as a *cold direct method* [69]. Whereas, if the particles do not possess any ability to structure the oil after dispersion, but a secondary liquid like water at low concentration needs to be added to the dispersion to obtain an oleogel but cannot be removed from the system, we refer to *semi-direct methods* [70].

This chapter aims to provide a comprehensive review and discussion of the different classes of gelators, their properties, and give some insights on their production methods, followed by a description of the oleogelation strategies and their current classification, along with some observations of their advantages and disadvantages. The chapter concludes with the proposal of new classification developed in our research group based on thermal treatment, electrical energy, and time required to form oleogels.

4.2 Production of Oleogelators

A non-exhaustive list of the most studied gelators is presented below, along with a brief description of their extraction/production methods and some of their properties (Table 4.1). The properties reported in the table may be of interest to the reader for understanding the methods described in Sect. 4.3 or when considering new research paths or industrial applications. For example, the degree of esterification (DE) is a facet specifically relevant for polysaccharides, as their gelling properties depend on the percentage or degree of esterified carboxyl groups [40, 71, 72]. Other properties such as the molecular weight of a gelator will affect the physical characteristics of a gel, as well as their interaction with different solvents and their time-dependent reactions with other materials in the system. Understanding the temperature dependence of a gelator's structure and its phase change (melting, crystallization, glass transition temperatures) is of great value, especially when considering the resulting oleogel's application, the limitations of temperature-labile compounds, or the sensory performance of the oleogel in food products.

During the early stages of experimentation and product development, it is recommended to familiarize oneself with the technical data sheet of the selected ingredients. Data sheets are commonly provided by the manufacturer and will aid the researchers, providing helpful information.

4.3 Oleogelation Methods

Among the available structuring agents for edible oils, a distinction can be made according to the type of strategy that is necessary for their dispersion in oil. In this section, we discuss the different oleogelation methods, grouping them into three categories: (1) addition of one or more gelators to oil—direct methods, (2) addition of gelators to a secondary solvent, typically water, that needs to be removed from the system to obtain an oleogel—indirect methods, (3) addition of gelators to oil that, not being able to structure oil themselves, require the presence of a secondary liquid at a low concentration to obtain an oleogel—semi-direct methods.

4.3.1 Direct Methods

The first developed and most studied oleogelation method involves the direct addition of the gelators to the oil, drawing inspiration from the traditional oil structuring method of having a colloidal network of triacylglyceride crystals, as present in most fat products that are available to the consumer [60]. Certain gelator molecules have the ability of crystallizing/self-assembling in the oil, allowing it to become semi-solid at room temperature. These gelators are typically LMWGs and can be added to the oil either as a single component or in mixtures, being addressed

Table 4.1 A list of the most studied oleogelators, their most common production methods, and their properties

Oleogelator type	Name	Extraction	Properties	References
Fatty acids	Mainly saturated fatty acids with carbon chain length between 16 and 22	Chemical hydrolysis using KOH followed by acid treatment. Enzymatic reaction of oils and fats with lipase	Amphiphilic. Melting temperature is dependent on saturation level, carbon chain length, and polymorphic form. The melting ranges for the neat components mainly used in oleogels are between 60 °C and 80 °C	[6–8]
Fatty alcohols (FAs)	Cetyl alcohol, stearyl alcohol, and other FAs	Obtained from natural sources rich in triacylglycerides (TAGs) or rich in wax esters through hydrogenation of fractioned and hydrolyzed TAGs	Amphiphilic but water insoluble when the molecular chain length is above 10 atoms. Melting temperature in FAs with 12 or lower atom chain length is around 16 °C, if above 12 atom chain length the melting temperature rises up to 72 °C (as in the case of 1-Docosanol)	[9–12]
Mono, di and triacylglycerides	Mainly saturated with carbon chain length of the esterified FA between 14 and 20	Glycerolysis through enzymatic reactions or through glycerol reaction with vegetable oils and fats, as well as hydrolysis with NaOH at high temperatures, followed by distillation	Amphiphilic. Its melting temperature is dependent on saturation level, carbon chain length, and polymorphic form. The melting ranges for the neat components mainly used in oleogels are MGs from 36 to70 °C, DGs from 60 to 67 °C, and TAGs from 54 to 68 °C	[13–15]
Phospholipids	Soy and egg lecithin	Extracted from crude oil through degumming, drying, and cooling. Egg yolk lecithin is obtained through several methods, including solvent, sub- and supercritical extraction.	Amphiphilic. Many phase transitions can be registered when applying heat from 40 to 200 °C	[16–19]

(continued)

Table 4.1 (continued)

Oleogelator type	Name	Extraction	Properties	References
Phytosterols and their esters	β-sitosterol	Phytosterol obtained from a wide array of plants (sunflower, pine bark, cocoa husks). Traditionally obtained through inefficient solvent extraction, apart from generating toxic waste. Other novel, more efficient, and economical methods exist, including microwave, supercritical fluid, ultrasonication, and Soxhlet extractions	Of special health appeal, due to its cholesterol-lowering and anti-cancer properties	[20–23]
	γ -oryzanol	Obtained from rice (*Oryza sativa L.*) bran. Extraction methods are comparable to those of β-sitosterol	Of special health interest, as it lowers intestinal cholesterol absorption, allowing for its elimination through feces	[23, 24]
Polysaccharides	Alginate	Extracted after a treatment with an alkaline solution from milled brown algae (*Phaeophyceae* genus)	Formed by a linear backbone of mannuronic and guluronic acids. Forms gels in the presence of cations	[25, 26]
	Carrageenan	Obtained from red algae by alkaline extraction and precipitation	Formed by sulfated and nonsulfated galactose and anhydrogalactose units. All carrageenans can be dissolved in water to form highly viscous solutions with pseudoplastic behavior. Forms gels with cations	[27, 28]
	Chitin	Chemically extracted from fungi, bacteria and shells of arthropods such as crabs and shrimps	Formed by linear backbone of N-acetylglucosamine units. Insoluble in water at acidic and neutral pH	[30–32]

	Ethylcellulose (EC)	Produced from alkali cellulose with ethyl chloride	Water insoluble. Undergoes a glass transition temperature (onset) around 130 °C	[33–35]
	Hydroxypropyl-methylcellulose (HPMC)	Product of the reaction of alkali cellulose with both propylene oxide and methyl chloride.	Soluble in cold water (below 40 °C) and surface-active. HPMC exhibits reversible thermal gelation from 55 to77 °C. Being non-digestible, acts as dietary fiber and improves the health of intestinal microbiota	[36–39]
	Methylcellulose (MC)	Produced from alkali cellulose treated with methyl chloride	Soluble in cold water (below 40 °C) and surface-active. MC has reversible thermal gelation at about 65 °C. Their solutions form a gel when heated up; the gels reliquefy when cooled down. Being non-digestible, acts as dietary fiber	[35, 39]
	Pectin	Obtained by acid hot extraction followed by precipitation of fruit by-products such as citrus peels and apple pomace	Water soluble. Formed by a linear backbone of galacturonic acid units and having a variable (high, above 50% and low, below 50%) degree of methylation	[26, 40, 41]
	Xanthan gum	Extracted from the precipitate of aerobic bacteria (*Xanthomonas campestris* and other *Xanthomonas* spp.) fermentation	Soluble both in cold and hot water. Formed by a linear backbone of glucose units with some branching	[26, 42, 43]
Proteins	Pea isolate	Obtained through alkaline solubilization of pea flour followed by isoelectric precipitation and recovery of the protein fractions	Mainly composed of albumins (water-soluble and of high nutritional value) and globulins (good emulsifying and gelling properties). Overall, pea proteins have lower gelling capacity and form a weaker gel structure than soy proteins	[45–49]

(continued)

Table 4.1 (continued)

Oleogelator type	Name	Extraction	Properties	References
	Whey protein isolate	Obtained from bovine's milk through ultrafiltration, ion exchange chromatography, and spray drying processes	Complex mixture mainly comprising β-lactoglobulin and α-lactalbumin, and immunoglobulins. Amphiphilic, with an isoelectric point of ~4.7	[49, 50]
Waxes	Beeswax	Obtained from bee (Apis mellifera) honeycombs through melting or chemical extraction with solvents)	Water insoluble. Heterogeneous composition comprising mainly wax esters (~60%, containing C16 fatty acids esterified with C24-C32 fatty alcohols), C27, C29, or C31 hydrocarbons (27%), C16 and C24 fatty acids (~8%), and C30 and C32 fatty alcohols (~6%). Broad melting event (from 40 to 70 °C) with melting peaks at 52 and 65 °C	[51, 52]
	Candelilla wax	Obtained from *Euphorbia antisyphilitica. Traditional method: 0.3% (v/v) sulfuric acid heat treatment. This method produces toxic gases and yields samples of lower quality that require further processing. Ecofriendly method: 2.4% (v/v) citric acid heat treatment*	Water insoluble. Heterogeneous composition comprising mainly C31 hydrocarbons (70–75%), wax esters (15%, containing C16, C18, or C22 fatty acids esterified with C18, C28, or C30 fatty alcohols), and C16 or C30 free fatty acids (~10%). Broad melting event (from 40 to 75 °C) with several melting peaks at 65 to 72.5 °C	[51, 53, 54]

	Carnauba wax	Obtained from the leaves of *Copernicia prunifera*. Depending on the quality of the leaves: through physical extraction (scrapping off or boiling and centrifuging the leaves) or solvent extraction	Low solubility in water. Heterogeneous composition comprising mainly wax esters (60%, containing C16, C18, C20, or C24 fatty acids esterified with C18, C30, or C32 fatty alcohols), C30, C32, and C34 free fatty alcohols (30–35%), and C16, C24, or C28 free fatty acids (around 6%). Broad melting event (from 79 to 87.5 °C) with melting peaks around 80 to 85 °C	[51, 56–58]
	Rice bran wax	Obtained from rice bran oil, through solvent dewaxing, defatting and bleaching	Water insoluble. Mainly composed of wax esters (>93%) containing C20–C24 fatty acids esterified with C24–C28 fatty alcohols, small percentage (<6%) of free fatty acids with carbon chain length between C16 and C24. A melting point can appear from 78 to 82 °C	[51, 57, 58]
	Sunflower wax	Obtained by the winterization sunflower (*Helianthus annuus*) oil refining.	Water insoluble. Mainly composed of wax esters (>95%) containing C20–C22 fatty acids esterified with C24–C28 fatty alcohols, small percentage (<5%) of free fatty acids with carbon chain length between C16 and C20. A melting point can appear from 70 to 77 °C	[51, 57, 59]

multi-component gelators. Up to date, the only HMWG which can structure oil through direct dispersion is ethylcellulose, due to the polarity of most HMWGs not being compatible with unsaturated fatty acid-rich oils. There are two types of direct oleogelation strategies: the hot direct method and the cold direct method.

4.3.1.1 Hot Direct Method

The hot direct method is a process in which the mixture of the oil with the gelator is heated to a temperature above the melting point of the gelator (or in the case of ethylcellulose, above its glass transition temperature), under constant agitation, to ensure full dissolution (usually 10–30 min). This is followed by a cooling phase, below the gelation transition temperature, in which the thermoreversible three-dimensional continuous network is formed, trapping the oil within the gel structure. The mechanical properties of the oleogel can be affected not only by the type of oil [73] and the type of gelator [51] and the ratio between them, but also by factors such as the cooling rate [74], and the mixture ratio when using multi-component gelators [75], among other factors. If an insufficient amount of gelators is used, or when the combination of gelators is incompatible and fails to work together, a gel is not obtained, but rather a viscous liquid or a dispersion of crystals in oil. The temperature at which the oleogel should be prepared depends highly on the type of gelator. For instance, monoglycerides usually require 70–80 °C heating. Waxes are a range of gelators with very different properties when retrieved from different sources and whose composition is highly variable, requiring heating in the 50–90+ °C range. Multi-component systems of β-sitosterol and γ-oryzanol require a heating phase of up to 80–90 °C [76]. Wang et al. [76] published a comprehensive review of the textural and rheological properties of LWMG-based oleogels, providing a useful knowledge pool about the preparation and properties of this type of oleogels. Ethylcellulose, as extensively explored in Chap. 7, requires a heating stage of above 140 °C to be dissolved in oil.

In order to structure oil, the gelator molecules that can be used via the hot direct method must first self-assemble through highly specific noncovalent interactions into primary particles through precipitation and/or crystallization (“bottom-up” nanofabrication) [77]. This phenomenon is followed by the assembly of individual molecules into supramolecular structures like crystal lattices, liquid crystals, micelles, bilayers, fibrils, and agglomerates, forming 3D networks capable of entraining the oil, resulting in a semi-solid material [78]. Typically, the intermolecular forces that drive aggregation are non-covalent, such as hydrogen-bonding, π–π stacking, dipole-dipole, and London dispersion forces [79]. These interactions stabilize the clusters and lead to the formation of a continuous network, which is influenced by anisotropic growth of supramolecular structures and anisotropic diffusion of molecules or clusters of molecules [78]. The balance between solubility and insolubility is the most important requirement and the key to obtaining a gel. To clarify, for a material to be used as a gelator, there must be a suitable balance between its affinity to the solvent (edible oil) and enough insolubility in the

solvent so that self-organization and assembly between gelator molecules are triggered (solubility limit of the gelator) [78]. The hot direct method relies on the interaction between solvent–gelator and gelator–gelator, as they play a central role in the formation of oleogels. Achieving optimal gelation seems to be the result of an optimal solvent-to-gelator ratio, although the direct effects of the solvent on the physical properties of the final oleogel are not well understood [79]. In general, a weak solvent–gelator interaction results in the prevalence of gelator–gelator interactions, which may lead to the formation of a continuous network, which is essential for the formation of an oleogel. Imbalances in this interaction can lead to the formation of other types of systems, *i.e.,* solutions or precipitates. The ability of a LMWG to gel a solvent has mostly been empirically explored, generally with a trial-and-error approach being used, which results in several failed trials.

Therefore, it is important to understand the interactions between the gelator and the solvent and reach an equilibrium of solubility and insolubility. The term "solubility parameter" was first coined by Hildebrand and Scott, in an attempt to predict solubility relations [80, 81]. The Hildebrand solubility parameter is a measure of the cohesive energy density of a substance, which is the energy required to separate the molecules in a material from each other. As such, the difference in solubility parameters for solvent–solute combinations is important in determining the solubility of the system. If the Hildebrand parameters of a solute and the solvent are similar, then the substance is likely to be soluble in that solvent. Adversely, if the Hildebrand parameters of the solute and the solvent are dissimilar, then the solute is likely to be insoluble in that solvent [82]. A limitation of the Hildebrand parameter is that it is unable to quantify the specific intermolecular interactions, which is part of the reason why the Hansen solubility parameters (HSP) were developed. These measure the total cohesive energy of a species as the sum of three individual energetic components (i.e., dispersion interactions, dipole–dipole interactions, and hydrogen–bonding interactions). In the same way as the Hildebrand parameter, the cohesive energy densities describe the ability of the solvent to solubilize the solute, or in this case, they describe the ability of a certain oil to solubilize a gelator, because they quantify the intermolecular forces that are required to overcome the gelator–gelator and oil–oil interactions. This equilibrium can be studied through the HSP and conveniently shown using the Hansen space, which allows for the visualization of the three fundamental intermolecular forces: dispersion, polar, and hydrogen bonding [83, 84]. If the HSP values of two compounds are close together in the HSP space, then the gelator is likely to be soluble in the oil. Some studies have been conducted using 12-hydroxystearic acid (12-HSA) and its derivatives as gelators, with an assessment of the impact of the hydroxyl group position in the formation of hydrogen bonds, as well as some other gelators [77, 79, 86–88]. These studies have helped to understand the gelation behavior of these compounds, by predicting their solubility in certain solvents. In addition, researchers have used these parameters to optimize known gelation systems, identify new ones, and develop tailored materials for the target applications [88, 89].

The diversity of forces acting on both gelators and solvents makes it difficult to accurately predict the outcome of a gelator–solvent combination. Though the use of

HSP can come up as a suitable way of predicting gelation behavior, other efforts are being made toward this goal. An interesting study by Cuello et al. [90] has proposed a Big Data solution to uniformize the existing data about LMWG and enhance the way knowledge is stored in this field. The authors collected data from heterogeneous sources and combined them into a unique, homogeneous platform, to allow the unification of current and newly obtained sources, as well as providing computing solutions to try and unravel the relationships between solvents and gelators. They demonstrated that the platform can be used to identify and characterize the key factors that influence the behavior of these gelators in food systems, and can provide insights on their future use. Essentially, this would be an application of data science and engineering to analyze and predict the most valuable cases to try in a laboratory setting, drifting away from the empirical approach that can overly consume time and resources.

4.3.1.2 Cold Direct Method

The cold direct method is carried out at ambient temperature or below, requiring only agitation for the dispersion of the gelator. The fact that it takes place at room temperature constitutes an advantage in comparison to the hot direct method, since temperature-induced oil oxidation is avoided. The method was first introduced by Patel et al. [91], who prepared oil dispersions of fumed silica by mixing hydrophilic colloidal silica particles with sunflower oil, followed by shearing the dispersion using a high-speed homogenizer, at room temperature. Oleogels were successfully formed at a concentration of 10 and 15% fumed silica, resulting in a 3D network based on the fractal aggregation of silica particles and consequent entrapment of oil. In contrast, hydrophobic fumed silica in oil exhibited low gelling behavior in oil, possibly due to the decrease in hydrogen bonding sites [92]. Since hydrophilic fumed silica has low solubility in oil, the attractive forces between silica particles are the drivers for the formation of the network and oil entrapment with minimal leakage [93].

Another approach explored the use of mercerized cellulose in the gelation of rapeseed oil [69]. Dispersions of cellulose powders from different botanical sources were prepared, with mass concentrations ranging from 5 to 40% in rapeseed oil. The dispersions were manually stirred for 2 min at room temperature. The intent of the authors when using such a wide concentration range was to conduct an empirical attempt at unveiling the critical value at which the dispersion exhibits solid-like behavior. It was concluded that though oleogelation critically depends on the cellulose content of the vegetable powders, the minimum gelling concentration and the textural properties are mainly governed by the size of the cellulose fibers, regardless of the botanical source.

4.3.2 Indirect Methods

Most food-approved polymers are inherently hydrophilic and are therefore unable to directly structure oil. Materials such as proteins and polysaccharides are regularly used in food applications and generally do not constitute an issue regarding legislation, depending on the specific type of protein or polysaccharide being used and its source. Indirect oleogelation methods are beneficial because they allow hydrophilic and amphiphilic polymers to be applied in oil structuring applications, usually starting out with water-rich systems and involving a series of procedures to remove water from the system.

4.3.2.1 Emulsion-Templated Methods

The indirect oleogelation strategies that start with the preparation of an emulsion are often grouped into the category of emulsion-templated methods.

Original Emulsion-Templated Method

The first indirect oleogelation approach was developed by Romoscanu and Mezzenga [63]. The authors suggested the application of a percolating 3D network of proteins for transforming oil into an elastic solid, without chemical modification. This method kicks off with the preparation of a monodisperse oil-in-water emulsion, where the oil droplets are stabilized by a cross-linked protein monolayer adsorbed at their interface. The procedure involves pumping the oil phase in the form of droplets from a pressurized tank into a β-lactoglobulin solution of 1% (w/w) that is coflowing via a glass capillary, creating a controlled environment. Due to the constant characteristics of the flow and break-off of the droplets, this method allows the fabrication of emulsions with a very high degree of monodispersity; however, there is the drawback of having a low output rate due to the sequential creation of the droplets. The emulsion is then left for one hour to complete protein adsorption onto the interface, and a washing procedure follows, with the aim of removing unadsorbed protein from the system. The cross-linking of the adsorbed β-lactoglobulin is then performed: this can be achieved either thermally, through the acceleration of cross-linking kinetics by keeping the emulsion at 80 °C for 10 min, or chemically, using glutaraldehyde. When applying chemical cross-linking with glutaraldehyde, the emulsion is poured into the same volume of 1% (w/w) glutaraldehyde, to avoid interparticle cross-linking. Another washing procedure follows to remove nonreacted glutaraldehyde, similar to the removal of unadsorbed protein. At this stage, there is the addition of a small amount of glycerol to increase its chemical potential and safeguard any internal stresses that can happen during the drying phase. This takes place at room temperature, where the emulsion is allowed to dry until the totality of the water has evaporated from the system, resulting in a fully

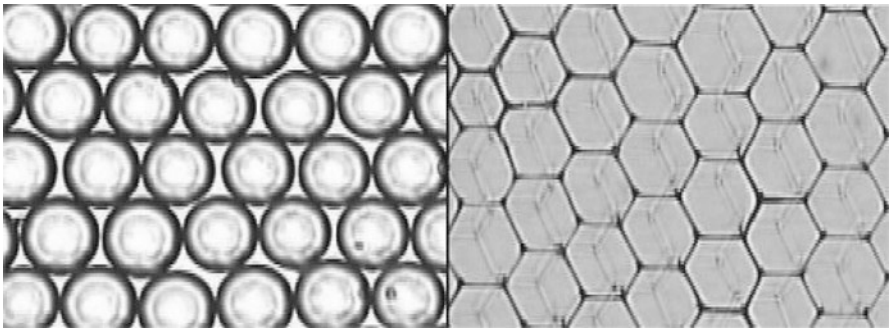

Fig. 4.1 Optical micrographs of an emulsion template (24 μm droplet radius) and a resulting two-layered thin film of gel exhibiting a polyhedral structure. (Figure reproduced from [63] with permission from the American Chemical Society)

transparent oleogel. The final structure resembles that of a dried foam, with a protein bilayer acting as the walls and the air being replaced by the chemically unmodified oil. The analysis of the oleogel's microstructure reveals a polyhedral arrangement with sizes comparable to the droplet size in the emulsion, as depicted in (Fig. 4.1) [63].

While the original method for preparing oleogels using emulsion templating was a breakthrough in the field, it has some disadvantages due to the use of chemically cross-linked proteins. Such proteins face many hurdles in being accepted for use in food products, including concerns about their safety, potential adverse effects on human health, and their impact on food texture and flavor [94]. Thermal cross-linking has comparable issues and also exhibits very slow cross-link kinetics, resulting in longer processing times and increased energy costs. Additionally, the cross-linking reaction can be difficult to control, and the complexity of the method made other authors shift to different approaches. Therefore, the method has undergone further developments with a focus on eliminating cross-linkers, leading to newly developed emulsion-templated methods, which are now more commonly cited as the reference, compared to the original emulsion-templated method here described.

Modified Emulsion-Templated Method

Unveiling the potential of cross-linked proteins for oil structuring by Romoscanu and Mezzenga [63] was the necessary foundation to discover what hydrophilic and amphiphilic polymers really have to offer in the structuring of hydrophobic oils. The procedure of using an emulsion template for the preparation of oleogels was later adopted and modified by Patel et al. [64], using the combination of a surface-active and a non-surface-active polysaccharides to generate oleogels. First, the authors attempted to establish a stable oil-in-water emulsion using only one surface-active polysaccharide (hydroxypropyl methyl cellulose—HPMC—or methylcellulose—

MC), with the results exhibiting a large droplet size and oil separation phenomena upon drying. On the other hand, a non-surface-active polysaccharide like xanthan gum was unable to stabilize the emulsion on its own, owing to its non-surface-active nature. However, the combination of one of the cellulose derivatives (HPMC or MC) with xanthan gum enhanced emulsion stability, exhibiting a more uniform droplet size with smaller droplets. These emulsions were prepared by dispersing oil in an HPMC or MC solution using a high-speed homogenizer followed by the addition of xanthan gum solution under continuous shearing. The emulsions were then oven-dried at temperatures between 50 °C and 80 °C until complete removal of water. The dried samples were then briefly sheared for 30 s to obtain an oleogel sample, which consisted of clusters of tightly packed oil droplets in oil continuous medium, with over 97% (w/w) of oil. The study investigated both the cellulose derivative type and its grade, observing their effect on the rheology of the emulsions, where lower viscosity polymer solutions resulted in stronger gels. This type of functionality was associated with the ability that the polysaccharides have to increase the stiffness of the interface, and hence contribute to the overall consistency of the emulsion (and, later, of the oleogel). This approach resulted in oleogels with a unique microstructure, featuring tightly packed oil droplets and no signs of oil leakage, as well as interesting rheological properties, such as high storage modulus, shear sensitivity, good thixotropic recovery, and thermostability.

While the use of polysaccharides provides advantages in terms of using GRAS ingredients, incorporating other biopolymers such as proteins has been acknowledged as advantageous. This is because proteins are label-friendly and have well-known additional health benefits that consumers value. Patel et al. [95] continued the work by modifying the original method by Romoscanu and Mezzenga [63], with the aim of using proteins and developing an alternative that does not require crosslinking. Instead, this alternative methodology by Patel et al. [95] benefits from the strong molecular complexes that result from protein–polysaccharide interactions at the interface. This was achieved by combining gelatin and xanthan gum, two edible natural materials that are commonly used in the food industry and are known for establishing hydrophobic interactions and non-Coloumbic interactions with the involvement of –NH and –OH groups. The oleogels were obtained by homogenizing sunflower oil in a gelatin solution, followed by the immediate addition of xanthan gum solution, under continuous shearing. The drying of the emulsion was carried out through both oven-drying and freeze-drying (FD), followed by a short step of shearing to create an oleogel (Fig. 4.2).

Once again, the stiffened interfacial membranes provide the oil droplets with better stability against stresses that the emulsion faces while drying. This kind of system was obtained by other authors using protein-polysaccharide complexes or multi-polysaccharide complexes, and in some cases, such a stable interface was already obtained by using proteins only. Tavernier et al. [96] first achieved an efficient structuring of oil using only unmodified proteins (soy protein isolate), and further attempts using 2% sodium caseinate also proved to be successful [97, 98]. However, the interactions between proteins and polysaccharides and the

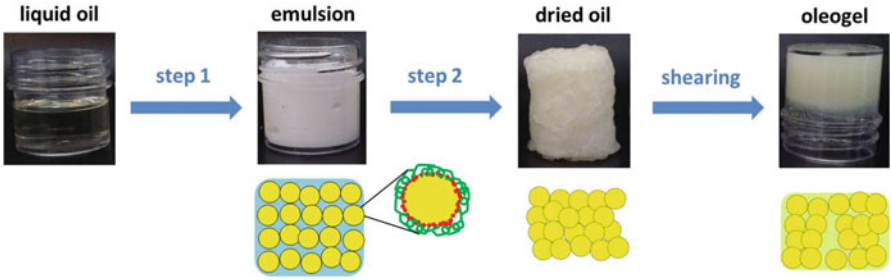

Fig. 4.2 Visual representation of the modified emulsion-templated method using protein-polysaccharide stabilization, through a combination of photographs depicting the result of each step of the process and sketches depicting the microstructure of the samples. Liquid oil is used to prepare a 60% (w/w) oil-in-water emulsion (step 1), followed by the removal of water through oven-drying or freeze-drying (step 2), and further shearing of the dried product (step 3), resulting in the formation of an oleogel. (Figure reproduced from [95] under the open access article as ACS AuthorChoice)

parameters that need to be fulfilled to achieve a sufficiently stable interface are still not fully elucidated [99].

Microcapsule-Templated Approach

The type of oleogels that are originated by LMWGs versus the type of oleogels that are originated by polymers is significantly different in terms of properties that they confer to food products. For example, LMWGs components that form crystalline conformations tend to result in oleogels with mouthfeel and processing properties that are more resemblant to fats. Adversely, polymeric gelators can provide other interesting textural properties such as firmness and consistency [68]. Coming up with a way that can combine these types of properties into one single oleogel has been attempted via direct strategies using multi-component gelator systems such as ethylcellulose-glycerol monoleate, [100], stearyl alcohol-stearic acid-ethylcellulose [101], and via indirect strategies using Pickering emulsions stabilized by zein–stearate complexes [102]. However, most of these attempts encompass harsh or energy-intensive processing (namely, heating at high temperatures or FD), which is not beneficial nor sustainably feasible in terms of process scaling-up and further commercialization. Thus, an effort was made by Patel [68] to execute a new approach using coated crystalline microcapsules to fabricate oleogels where both fat crystals and polymer sheets cooperate in providing structure to the system (Fig. 4.3). Microcapsules were prepared using palm stearin, a common hard stock fat; the procedure starts with the development of an oil-in-water emulsion stabilized by MC and an immediate dilution of the emulsion in ice-cold water to trigger immediate solidification and creaming of the oil droplets, coated with methylcellulose. These microcapsules were then recovered and dried at mild temperatures (30–32 °C). The microcapsules were then dispersed in oil for the preparation of

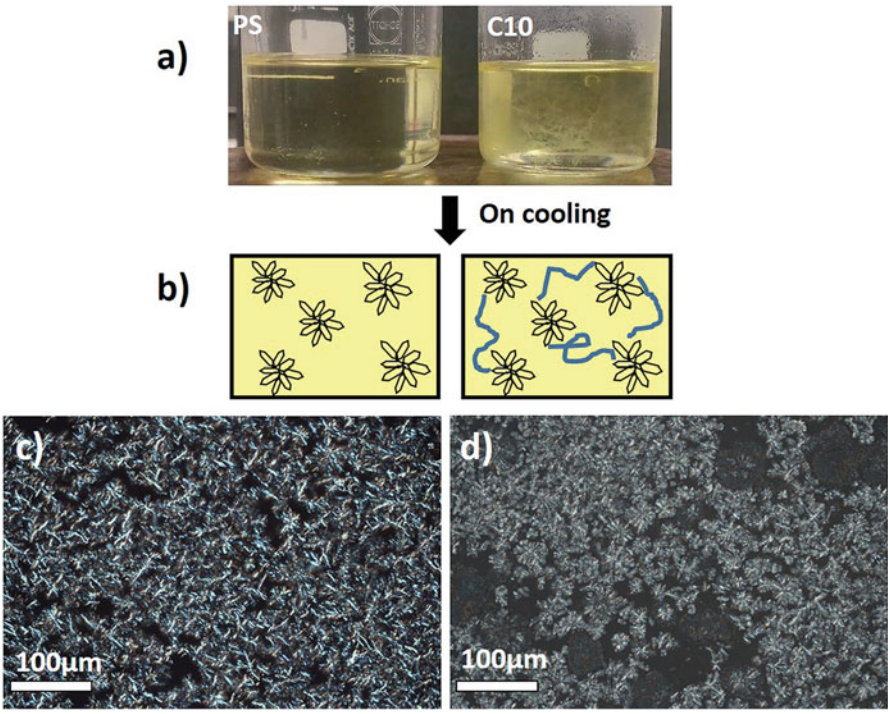

Fig. 4.3 Visual depiction of the oleogel preparation process, represented through a combination of photographs, sketches, and polarized light microscopy images (**a**–**c**). The comparison showcased in the figure is between two types of oleogels: one prepared from unprocessed palm stearin, on the left (**a** left, **b** left, and **c**), and the other from palm stearin capsules made using an emulsion that contained 10% (w/w) oil phase, on the right (**a** right, **b** right, and **d**). The crystal structures in (**b**) left are representative of palm stearin crystals, whereas (**b**) right shows the same crystals and MC strands. (Figure reproduced from [68] with permission from Elsevier)

oleogels; the dispersion was heated up to 70 °C, leading to the melting of the capsules and the dispersion of the capsule coats as polymer strands. The system was then cooled down to room temperature, forming a network of crystallized palm stearin and MC strands. When compared to an oleogel structured using only palm stearin, the microcapsule approach presented advantages such as a controlled crystallization of palm stearin in discrete spherical units, as opposed to uncontrolled growth and aggregation characteristic of pure palm stearin oleogels.

Oleosome-Templated Approach

Oleosomes are microbodies that can be found abundantly in oleaginous seeds and fruits, essentially being naturally pre-emulsified oil. Functionally, they are important for lipidic storage, serving as an energy source and protection against environmental stresses. Structurally, they consist of oil droplets that are encapsulated and stabilized

by a unique protein/phospholipid membrane [103]. These can provide an excellent medium for forming gel-like structures; despite that, there are very few applications of oleosomes in the oleogel field.

Mert and Vilgis [104] first explored this possibility by extracting natural oleosome structures from oil-bearing plant materials (particularly, hazelnut) and stabilizing them with xanthan gum or pectin. These hydrocolloids were used first for the stabilization of natural oleosome suspensions using an electrostatic deposition technique, that has been shown to improve aggregation stability of emulsion droplets when exposed to environmental stresses such as dehydration. Then the water was driven off the system via FD, obtaining a dry product that was further sheared, until a gel structure was obtained [104]. The driving force behind the establishment of this type of oleogel is the complexation between the oleosin proteins that are present in the oleosome membrane and the polysaccharides, following the trend of other similar oleogelation systems that have been mentioned earlier in this section (4.3.2.1). This could be considered a more sustainable and economic option, considering the use of natural oil bodies that do not have to be artificially fabricated but instead extracted from oleaginous plants. The electrostatic interactions between oleosomes and polysaccharides have been studied in systems containing soybean oleosomes, sodium alginate, and xanthan gum, to further understand said interactions and amplify their application in the oleogel field [105].

4.3.2.2 Foam-Templated Method

During the same period that the modified emulsion-templated method was developed, the same research group explored the development of an alternative method. Patel et al. [106] reported for the first time a foam-templated approach using a water-soluble polymer and low-temperature processing. The foam template is turned into a porous cryogel via FD to remove water, resulting in a material with excellent oil sorption properties. Cellulose derivatives such as HPMC or MC can be very intuitively suitable candidates for this kind of approach: these derivatives are synthesized by substituting the hydroxyl group of cellulose with hydroxyl propyl or methyl groups. This imbues the molecules with a certain degree of hydrophobicity, conferring them an amphiphilic character and a certain degree of surface activity, which makes it easy to incorporate air into the HPMC solution [107].

The method developed by Patel required the preparation of an HPMC solution first, by dissolving it in water in a concentration of 1–2% and overnight mixing. The solution was further processed using a high-speed homogenizer operating at 11,000 rpm; this process aerates the system and results in an aqueous foam, presenting an average bubble size of less than 150 μm. The obtained foam was then subjected to FD, originating a porous cryogel. The oleogel formation ensues, by absorbing high, weighted quantities of sunflower oil into the dried cryogels and allowing the system to rest overnight. At this stage, as the cryogel was formed only by HPMC and without the use of any crosslinking, the oil was expected to flow through the entire structure and hence be quickly absorbed, but not tightly bind to the

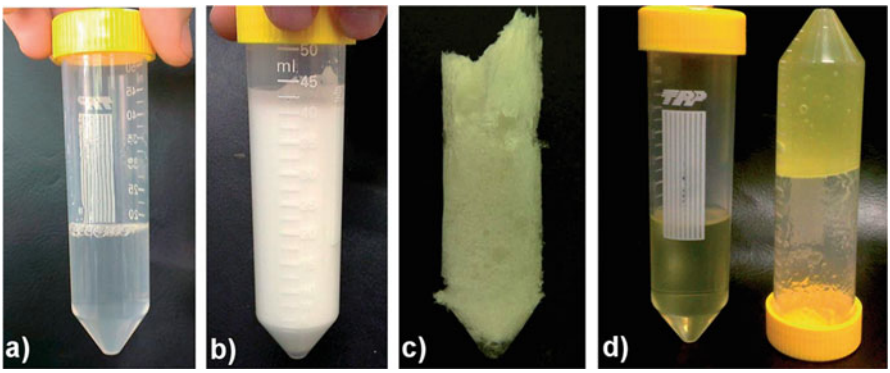

Fig. 4.4 Sequential photographs of the foam-templated method stages: (**a**) 1% (w/w) hydroxypropyl methylcellulose (HPMC) (4000 cps) solution; (**b**) aqueous foam formed by aerating HPMC solution; (**c**) porous cryogel obtained by removal of water by freeze-drying; and (**d**) comparative pictures of sunflower oil on the left and organogel (with 98% (w/w) oil) formed using the cryogel on the right. (Figure reproduced from [106] with permission from the Royal Society of Chemistry)

structure, having a high risk of oozing out with minimal pressure. As such, the material was then sheared at 11,000 rpm using a high-speed homogenizer to obtain oleogels and prevent the release of oil (Fig. 4.4). This way, the polymer sheets were uniformly dispersed in the oil-continuous phase, physically trapping the oil, and preventing leakage. The weight of the added oil was calculated at about 98–99 times the weight of the cryogel. Later approaches used this foam-templated method as a guideline and focused on broadening the range of gelators suitable for this kind of methodology to include proteins. So far, a combination of gelatin and xanthan gum [108] and a combination of pea/faba protein and xanthan gum [109] have been successfully used to prepare oleogels through a foam template. These two studies have in common the fact that a polysaccharide was necessary to improve foam stability. Another study with rice bran protein successfully resulted in oleogels [110]; this approach required a pH adjustment step to adjust surface activity and allow for a faster adsorption on the interface.

The advantage of the foam-templated method is that high temperature is not needed, which could lower the risk of lipid oxidation and non-desired flavors. However, it is a method that consumes high amounts of energy and time, due to the FD process.

4.3.2.3 Hydrogel-Templated Method

Solvent Exchange Method

After the potential of proteins was revealed through the emulsion-templated method with crosslinking, as described above, de Vries et al. [62] further developed the applicability of proteins as sole gelators for oil structuring *via* a solvent exchange

procedure. First, a heat-set protein hydrogel was created using whey protein isolate (WPI) powder; they were prepared by heat denaturation of the proteins, using a temperature-controlled water bath at 85 °C for 30 min. The gels were then allowed to cool down to room temperature and stored overnight at 4 °C. The exchange of water retained in the protein matrices for sunflower oil was made following a stepwise approach, using an intermediate solvent. For the intermediate solvent, tetrahydrofuran (THF) or acetone was used, considering that they are miscible both with water and sunflower oil. The hydrogel was cut into cylindrical pieces that were placed onto mesh metal buckets and then immersed for 8–12 h into the next solvent under continuous stirring of the solvent, and so forth. The succession of immersions goes from a solution of 30% (v/v) intermediate solvent in water, proceeding with 50% (v/v), 70% (v/v), and two subsequent immersions in 100% (v/v) intermediate solvent, following the above-mentioned stepwise approach. After the full replacement of the water with the intermediate solvent, a similar stepwise approach was applied using solutions of 30% (v/v), 50% (v/v), and 70% (v/v) sunflower oil in intermediate solvent and 100% (v/v) pure sunflower oil, to reach full substitution of the intermediate solvent with oil. The result oleogels were removed from the mesh metal buckets and blotted dry with tissue paper (Fig. 4.5). Up to 91% (w/w) oil could

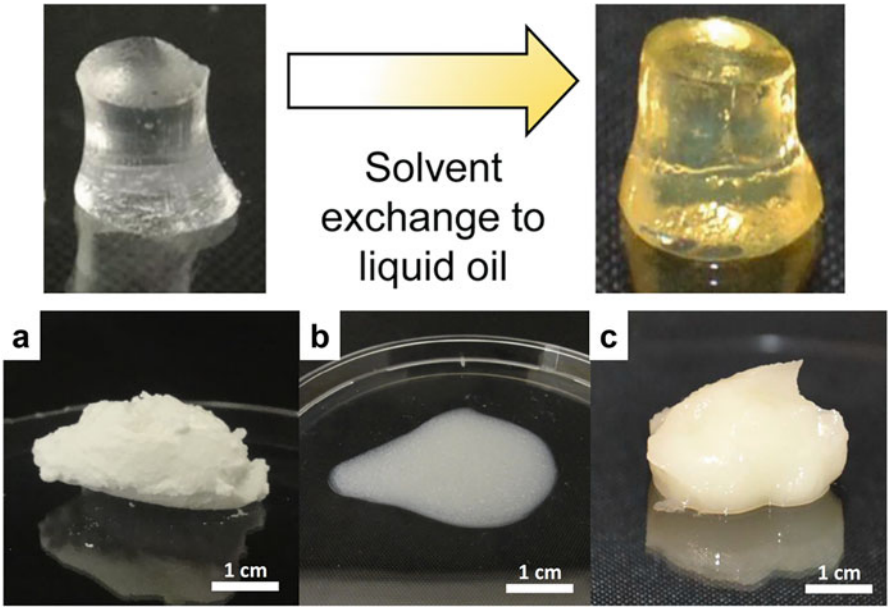

Fig. 4.5 On top, the appearance of 15% WPI hydrogels (left) and respective oleogels (right) after the solvent exchange. (Reprinted from [62] with permission from the American Chemical Society). On the bottom, (**a**) the appearance of heat-set WPI aggregates after centrifugation; (**b**) dispersion of freeze-dried protein aggregates in sunflower oil; and (**c**) resultant protein aggregate-based oleogels obtained through a solvent exchange method. (Reprinted from [111] with permission from Elsevier)

be incorporated into the system with a residual amount of water (under 1% (w/w)), which exhibited a Young's modulus above the respective hydrogels by 2 orders of magnitude.

However, the research group acknowledged that the preparation method, though effective, had limited flexibility to alter the rheological properties of the final protein oleogels. The oleogels were much stiffer and more brittle than the original gelling system (hydrogel). In an attempt to create a system that allowed for better tuning of its rheological properties, they decided to extend their previous work and explore the possibility of using protein aggregates of colloidal size to structure oil, while comparing them to their hydrogel counterparts [111] (Fig. 4.5).

This alternative process developed by de Vries et al. [111] starts with the preparation of a protein stock solution of 4% (w/w) WPI. The mixture was then refrigerated overnight to ensure that the protein was fully hydrated and the pH was adjusted to 5.7 the next day using a 1 M HCl solution. The solution was heated at 85 °C for 15 min to denature the protein, resulting in a weak gel, which was easily broken into smaller pieces. These pieces were homogenized using a high-speed homogenizer for 3 min at 13,000 rpm. The protein aggregates were collected by centrifugation and washed twice with demineralized water to remove any remaining soluble protein. For preparation of the oleogels, the WPI aggregates were dispersed in acetone and then centrifuged to collect the pellet containing the protein. This process was repeated once more using acetone to ensure water removal and twice in sunflower oil. The resulting pellet was diluted with sunflower oil, and excess acetone was allowed to evaporate overnight. The mixture was then centrifuged to increase the concentration of protein aggregates and form a gel. An alternative method of dispersing the protein in oil was also tested using FD. The resulting powder was dispersed in oil and centrifuged to increase protein concentration. As opposed to the first approach, instead of using a protein backbone to structure oil, the proteins are viewed as building blocks to the system rather than a fixed network. This study found that efficient network formation was achieved through hydrophilic interactions between the aggregates, even when in a hydrophobic oil medium. Typically, the network formation of colloidal particles depends on both particle–particle and particle–solvent interactions, as explored in Sect. 4.3.1. Therefore, it must be considered that changes at the level of the solvent can manipulate the network formation and its resulting rheological properties. Further works focused on using this protein aggregate-solvent exchange while varying the polarity of the oil, establishing a relationship between the polarity of the oil and the gel strength [112].

Aerogel-Templated Method

The aerogel-templated method was first described by Manzocco et al. [61]. In this method, a hydrogel made of κ-carrageenan was converted to an alcohol gel via a stepwise solvent substitution (water to ethanol), using the approach described by de Vries et al. [62] and in the previous section. The obtained alcohol gel was then dried under a continuous flow of supercritical carbon dioxide (SC-CO_2) at 11 ± 1 MPa and 45 °C. After 8 h SC-CO_2 drying, a monolith aerogel was obtained. Subsequently, the

aerogel was soaked in sunflower oil which diffused inside the aerogel porous structure and an oleogel was formed. Carbon dioxide transits from liquid or gas to a supercritical fluid above 31.1 °C and 73.8 bar (or 7.38 MPa), giving it low viscosity and high diffusivity like gasses and high density like liquids. These properties make supercritical fluids excellent and versatile solvents. Upon returning to ambient pressure, CO_2 transits to a gas state, leaving the material that has been in contact with, without any traces. The κ-carrageenan aerogel obtained by Manzocco et al. [61] was able to absorb a mass of oil between two and four times its original mass, leading to an oleogel composed of around 20–25% biopolymer and the remaining fraction of sunflower oil. These oleogels were characterized by high firmness (between 100 and 300 N upon compression) due to the dense and compact aerogel structure, and their oil holding capacity was between 60% and 80% (expressed oil upon centrifugation compared to the original oil mass in the oleogel).

From this original work, the same research group has published a series of articles demonstrating that the properties of oleogels obtained with SC-CO_2 dried aerogels can be greatly tailored. Indeed, by adding lettuce as a filler into κ-carrageenan gels, one can reduce the firmness of the resulting oleogel and increase the mass of absorbed oil up to 15 times the mass of the initial aerogel [113]. The same authors showed that fresh-cut salad waste-based aerogels, cellulose aerogels, as well as WPI aerogel particles can be used to form an oleogel [115–117]. In the latter case, the resulting oleogel contained 15% particles and 85% sunflower oil and resulted in a moldable material with rheological properties that are typical of a gel [115] (Fig. 4.6). Finally, these authors also demonstrated that oleogels structured through protein aerogel particles one can steer oil and protein digestibility [117]. Particles of aerogels made of starch were recently employed by Alavi and Ciftci [118] to obtain a moldable oleogel. The addition of chitosan to starch prior to forming an aerogel improved considerably the oil structuring ability and the mechanical properties of the resulting system.

Although SC-CO_2 drying is a great tool to obtain aerogels for oleogel preparation, the need for specialized and tailor-made equipment, as well as long processing times for the aerogel preparation (48 h to one week to replace water with ethanol to obtain an alcohol gel and 8 h of drying to obtain an aerogel), led researchers to look for alternative aerogel production methods like FD. Even if there is still a debate on the

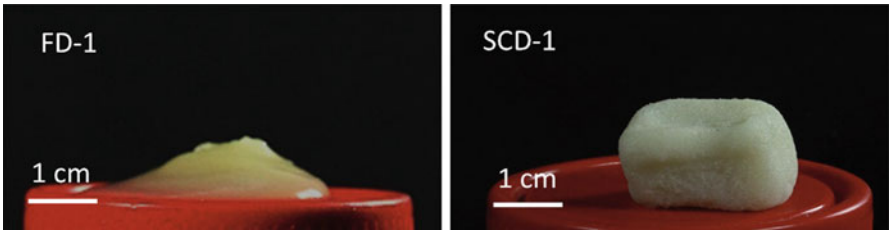

Fig. 4.6 Oleogels obtained with freeze-dried (FD-1) and supercritical CO_2 dried (SCD-1) whey protein aerogel particles dispersed in sunflower oil. The composition of FD-1 is 31% particles and 69% oil, and that of SCD-1 is 15% particles and 85% oil. (Figure reproduced from [115] with permission from Elsevier)

definition of aerogels based on the preparation technique [119], in this paragraph, we consider porous materials as defined by Smirnova and Gurikov [120] as aerogels, regardless of the preparation method. In FD, water-based gels/materials are directly converted into porous materials after a drying step under vacuum at low temperature (usually −20 – −60 °C for 24–72 h), preceded by the freezing of the original material (usually at −80 °C to promote the formation of small ice crystals, which lead to smaller pores during drying). Some studies highlighted that if the same hydrogel is used for FD and SC-CO_2 drying, the structure of the resulting aerogels is more collapsed in FD aerogels, leading to mechanically weaker oleogels or showing a lower ability to absorb oil [114, 115] (Fig. 4.6).

However, these limits can be solved by improving the structure of the starting hydrogel. On this topic, Zhao et al. [121] added carboxymethyl chitosan (CMCS) to WPI to form heat-set modified hydrogels, which were subsequently FD to form an aerogel. The presence of up to 0.75% CMCS in the aerogel led to the formation of oleogels (after immersion of aerogel for 6 h in soybean oil) which were able to absorb oil up to five times the mass of the initial aerogel and retain more than 96% of the initial oil upon centrifugation. In addition, the oleogel obtained had better oxidative stability and high astaxanthin bioaccessibility compared to bulk oil. In another study, Chen and Zhang [122] developed aerogels by applying FD to hydrogels composed of alginate/soy protein conjugates obtained through the Maillard reaction. Oleogels were obtained by immersing the aerogel for 6 h in corn oil, which was able to absorb oil at 10.9 times its initial mass and retain 40% of it upon centrifugation. Finally, Li and Zhang [65] developed oleogels by dispersing gelatin-based aerogels in camellia oil. Aerogels were obtained through FD of either gelatin hydrogels or short gelatin electrospun nanofibers in water. However, we report here data related to the first case, whereas data related to oleogels obtained using electrospun nanofibers will be discussed in the following section. The authors showed that all the studied characteristics and properties of the oleogels were dependent on the concentration of gelatin in the starting hydrogel. In particular, aerogels were able to absorb a mass of oil comprised between 20 and 100 times their initial mass and retain between 30% and 60% of the initial oil upon centrifugation. Moreover, the obtained oleogels showed thixotropic recovery between 76% and 94%, and a free fatty acid release during in vitro digestion between 40% and 60%.

4.3.2.4 Electrospun Nanofiber-Templated Method

The last indirect method developed for oleogel production we present in this chapter is based on electrospun nanofibers. Electrospinning is an electrohydrodynamic process where micro- and nanofibers are drawn out from an electrified polymer solution and dried during their travel to a grounded collector. A typical electrospinning setup consists of a high-voltage power source, a syringe pump, a spinneret (typically a needle with a blunt tip), and a conductive collector [123]. However, needleless electrospinning devices are also emerging [124]. Different food grade high molar mass biopolymers like zein, gelatin, whey protein, starch, cellulose derivatives, carrageenans, alginate, pullulan, dextran, chitin, and chitosan, to name a

few, have been electrospun forming nanofibers with diameters in the range of few hundreds of nm (generally below 1 μm) [123, 126–128]. Biopolymers used in electrospinning do not need to possess any emulsifying, foaming, and thickening properties like those used in the other indirect methods, making the production of electrospun-based oleogels a more versatile indirect method for oil structuring.

Most of the research on developing oleogels from electrospun nanofibers is on the structuration of castor oil for lubrication purposes [66, 129–131]. In these works, the electrospun nanofibers were obtained by applying an electric field of 0.4–1.5 kV/cm and using solutions containing mixtures at different concentrations and ratios of Kraft lignin and cellulose acetate, and of polyvinylpyrrolidone and Kraft lignin [128, 130]. Electrospun nanofibers were dispersed at a concentration of 5–30% (w/w) in castor oil using gentle mixing. The resulting oleogels showed rheological and tribological properties dependent on the concentration of the nanofibers in the oleogel and the composition of the nanofiber. However, in general, the obtained oleogels showed rheological and tribological properties like commercially available lubricating greases made from metallic soaps and mineral oils [66, 129–131].

On the other hand, to the best of our knowledge, the only published example of edible oleogels obtained using electrospun nanofibers was recently published by Li and Zhang [65]. The authors developed gelatin-based electrospun nanofibers using an electric field of around 1.3 kV/cm applied to gelatin in an acetic acid solution. Following, nanofibers were added to liquid tert-butanol at different concentrations and homogenized using a high-speed homogenizer to reduce their length. The solvent was then removed using FD. The final system was an aerogel formed by short electrospun nanofibers, which were immersed in camellia oil and formed an oleogel. Although this method is the result of the application of two indirect methods and could be classified as a hybrid method, here we decided to group it in this category since the main structure of the oleogel is given by the nanofibers. The authors proved that oil absorption and retention, as well as rheological properties and digestion profiles of oleogels, were correlated with the concentration of nanofibers dispersed in tert-butanol before forming the aerogels. More specifically, aerogels were able to absorb a mass of oil between 60 and 125 times their initial weight and retain between 60% and 80% oil upon centrifugation, which exhibited better oil absorption and retention compared to aerogels obtained using gelatin hydrogel as a starting system for aerogel production (more details in the previous paragraph). On the other hand, the oleogel obtained using nanofibers showed a thixotropic recovery between 36 and 79% and a release of free fatty acids during in vitro digestion between 40 and 50%.

Although electrospinning is a promising technology to obtain nanofibers for oil structuration, it is still affected by some limitations such as possible blockages in the spinneret, residual solvents in the nanofibers, and long processing times [131]. To overcome these problems a novel open-surface needle-free electrospinning device featuring one or multiple focused ultrasonic transducers, namely ultrasound-enhanced electrospinning (USES) has been developed [132–135]. We recently developed a new, cold method to obtain oleogels using a mat of USES nanofibers. The nanofibers were formed using a standard polymer, polyethylene oxide. After dispersing the nanofibers in oil and subjecting the mixture to cryo-milling, oleogels

could be formed in rapeseed, walnut, and flaxseed oils at nanofiber concentrations above 10%. The oleogels were formed by a jammed dispersion of nanofiber mat fragments, exhibited excellent thixotropic recovery, and the stiffness of the oleogel was proportional to the nanofiber concentration and the unsaturation level of the fatty acids composing the oil [67].

4.3.3 Semi-Direct Method

The semi-direct oleogelation method is a recently developed technique that uses gelators or particles that can be dispersed in oil but require a secondary liquid to form an oleogel. The term "semi-direct" was chosen because this method features characteristics of both direct and indirect methods: direct addition of gelators or particles to oil, and the use of a secondary liquid like water. However, unlike in the indirect methods, the water cannot be removed from the system, or the self-supporting structure of the oleogel is lost. Therefore, in the semi-direct method, oleogels are formed by mixing the particles and the two liquids. Currently, there is only one type of method that can be classified as "semi-direct," i.e., capillary suspensions. In this method, insoluble particles are first added to the oil at concentrations ranging from 10% to 50–60%, forming an oil-particle dispersion. Water or aqueous solution is then added, usually, in the concentration range of 2–20% of the final system and an oleogel is formed upon mixing. Capillary suspensions are a particular case of ternary particle–liquid–liquid systems. Indeed, depending on the relative ratio among particles and liquids, other systems like Pickering emulsions, bigels (bicontinuous gels), spherical agglomerates, and granular materials, can be obtained (Fig. 4.7) [135].

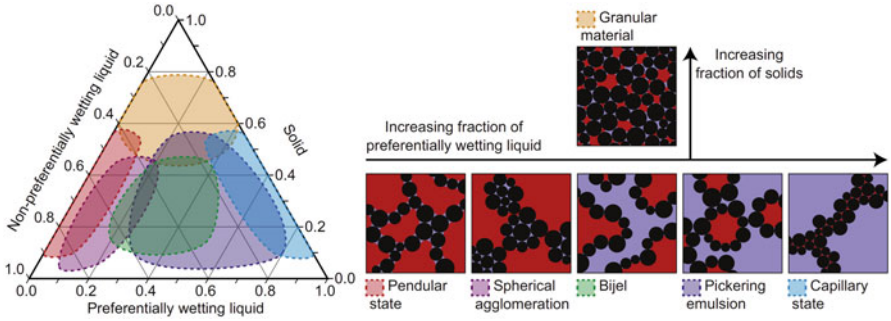

Fig. 4.7 On the left, a ternary diagram of particle–liquid–liquid systems depicting estimated areas of stability for different states based on the relative volume fractions. On the right, a schematic representation of each state depicted in the ternary diagram. Capillary suspensions occupy the perimeter of the ternary diagram, where one of the secondary liquids appears as a minor phase across various particle volume fractions. (Figure reproduced from [135] with permission from Elsevier)

The formation of liquid bridges among particles in capillary suspensions results in the structuring of the system through capillary forces. The strength of these forces is influenced by the dimension of the particles, their distance, the interfacial tension between the two fluids in contact with the particles, and the three-phase wetting angle that the secondary liquid forms against the solid surface in presence of the bulk liquid [135, 136]. Capillary suspensions comprise two different states: pendular and capillary, which depend on the wettability of the particles with respect to the two immiscible liquids used in the ternary system. In particular, the pendular state refers to ternary systems where the secondary liquid preferentially wets the particles that are dispersed in a non-preferentially wetting liquid. The secondary liquid binds individual particles together forming pendular bridges (Fig. 4.7). In the examples reported below, most of the oleogels are formed through capillary suspensions in the pendular state, since the particles are mainly hydrophilic and are dispersed in oil, where water is used as a secondary liquid. On the other hand, capillary state refers to systems where particles are dispersed in a bulk liquid that preferentially wets them, and a secondary liquid that does not preferentially wet the particles is added to the system. The secondary liquid fills the gaps among particles forming clusters that are kept together by the capillary forces from the bulk liquid (Fig. 4.7) [135, 137]. The capillary suspension states can be differentiated based on the saturation (S) level of the wetting liquid, expressed as the ratio of the volume of wetting liquid to the total liquid volume of the system. In the capillary state, the S value approaches unity, while in the pendular state, it is close to zero. Regardless of the capillary suspension state, a transition from a liquid-like unstructured suspension to a gel-like material is always observed [135].

One of the earliest studies on edible oil structuring through capillary suspensions was described by Hoffmann et al. [136]. In this study, the authors used starch granules and cocoa particles at 30–35% volume fraction and 10–30% water to structure sunflower oil. The rheological properties of the system were dependent on particle and water volume fractions, and the addition of glycerol to water increased gel strength. However, the order of secondary liquid addition did not influence the rheological behavior of the system, leading to similar results whether the water was added to the starch-oil suspension, or it was absorbed onto the dry starch granule surface. In another early study on oil structuration, Mustafa et al. [70] used particles derived from agri-food waste such as tomato peels and spent coffee grounds to structure peanut oil. By using a 25% volume fraction of particles in oil and adding 17–57% volume fraction of water relative to the oil using a high-speed homogenizer, a transition from a dispersion to a semi-solid gel-like material was observed. The hydrophilic character of the particle surface led to the establishment of capillary bridges upon water addition, arranging the particles into a three-dimensional network that entrapped the oil phase. The authors demonstrated that the resulting material stiffened with increasing water content (up to a certain point) and with decreasing particle size through high-pressure homogenization [70].

Following these first studies on the use of capillary bridges in oil structuring, other recent works showed the effectiveness of proteins, cellulose particles, and fibers in semi-direct oleogelation methods, although proteins and fibers have been

typically used in indirect methods, whereas cellulose particles have been used in hot and cold direct methods [69, 138]. In particular, hydrophilic modified zein particles (size of ~200 nm), heat-set whey protein isolate particles, cellulose particles with an average size of 25 μm, particles from fiber-rich fractions of yellow pea such as epidermal pea cell wall (average size of 20 μm) and pea hull (average size of 300 μm) were used to structure soybean, sunflower, algal, castor, and medium chain triacylglycerol (MCT) oils [140–142]. In general, 10% to 40% particles were dispersed in oils, followed by the addition of water at concentrations between 2% and 30% and the system was mixed using ball milling, high shear mixing, or magnetic stirring. Eventually, all systems formed oleogels at an oil-water-particle ratio that allowed a capillary suspension in the pendular state to be formed. When full pendular bridging (also called funicular state) among particles was formed, *i.e.,* each particle was interconnected with neighbor particles through water bridges and participated in network formation, stiff oleogels were produced [139]. Oleogel rheological properties could be further modulated by modifying ionic strength, solid content, and pH of the secondary liquid [139, 140].

Finally, as seen from the above examples, the selection of particles and liquids is fundamental to obtain an oleogel through capillary suspensions and to be able to tailor its rheological properties. On this topic, Jarray et al. [142] introduced a new approach that can predict the formation of capillary suspensions in the pendular state and their rheological properties using the HSP computed from molecular dynamics simulations. The authors elucidated through simulations and experimental work that the gel strength of capillary suspensions obtained with hydrophilic silica particles arises from the intermolecular interactions of its components, where the interfacial tension between the bulk and secondary liquid drives the gel strength up to a certain limit, after which the secondary liquid–particle polar interactions and hydrogen bond formation play a major role. The approach proposed by Jarray et al. [142] could potentially be extended to any particles. Furthermore, by using the HSP theory, one can select the proper secondary liquid, which can lead to the formation of capillary suspensions and calculate the resulting gel strength, reducing the need for extensive experimental work.

4.4 New Classification of Oleogels

As discussed in Sect. 4.3, oleogel preparation methods can involve water or other solvents, heating and cooling cycles, drying procedures, and gelators with different molecular weights. However, the difference among oleogelation methods can also be explained by taking into consideration (a) heat energy that the oil is subjected to, (b) the overall electrical energy consumed by all devices during oleogelation, and (c) overall oleogelation time. These three factors are imperative in oleogel production since they are important criteria affecting oxidative and/or storage stability of the oleogels, as well as their sustainability, upscaling ability, and overall production cost. To make use of the benefits of oleogels in society, their production must be

scaled up from the laboratory to an industrial level. Achieving this requires contextualizing the classification of oleogel preparation methods within an industrial framework. However, the conventional classification of oleogels based on either the molecular weight of the gelators (LMWGs *vs.* HMWGs) or the oleogelation methods (direct, indirect, and semi-direct), does not provide pertinent information for industrial applications.

In a recently published article [143], we discussed the importance of these three industrially relevant factors—overall heat, electrical energy, and time—in obtaining a new classification system for oleogel preparation methods. To this aim, we calculated these three parameters for 216 laboratory-conducted oleogelation cases retrieved from the literature. The overall heat that the oil is subjected to during oleogelation was calculated by integrating the time-temperature (TT) profiles. The overall electrical energy consumption was calculated by summing the electrical consumption of all devices used during oleogel preparation. The overall time was calculated by summing the time necessary for every single action during oleogel preparation. Each oleogel preparation procedure was then plotted in a 3D space where the three axes corresponded to heat, electrical energy, and time. Each oleogel preparation case was distributed in a different position within the scatter plot and different groups were visible. By applying the K-means clustering algorithm followed by the scree plot analysis, we were able to determine an optimal number of clusters. From this clustering, we developed a new oleogel classification where each oleogel preparation case (type of method, gelator concentration, etc.) was assigned to a new class based on its level of input: low, medium, or high (Fig. 4.8). The low-input approaches require low inputs (heat, electrical energy, and time), and are the optimal cases in terms of oxidative stability, sustainability, and industrial relevance. The medium-input approaches need a medium amount of at least one input, thereby making them potentially unattractive; however, they can still be considered when other options from the low-input approaches are not applicable. The high-input approaches require a high amount of at least one input. These methods are currently the least attractive ones.

Our new classification challenges the commonly held belief that oil subjected to hot direct methods undergoes more severe thermal cycles and higher heat exposure than those processed *via* indirect methods. For example, the emulsion-templated approach using oven-drying (a common indirect method) subjects the oil to higher heat treatment than some hot direct methods. Instead, we propose that oleogelation methods should be evaluated on a case-by-case basis.

The results of our novel classification also highlighted that scaling up oleogelation requires considering additional aspects that usually were not considered in the laboratory-conducted oleogelation cases, such as proper control of the cooling rate, as it significantly affects the heat energy that the oil is subjected to. The cooling rate is also a crucial factor in achieving consistency in physical properties (e.g., minimum gelation concentration, melting temperature, melting enthalpy, yield stress, solid phase content, and oil binding capacity) of oleogel during scale-up [144]. A constant surface area-to-volume ratio was recently suggested to be a key factor in scaling up oleogel production. By keeping the ratio constant, authors

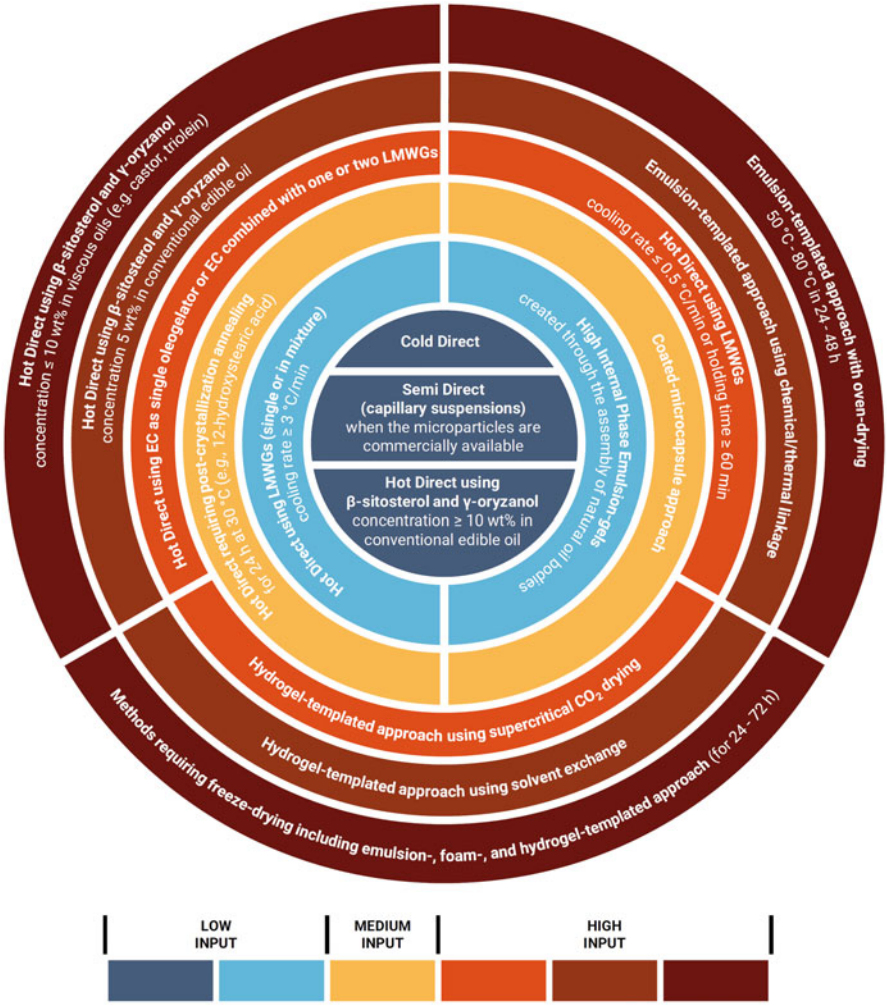

Fig. 4.8 Schematic visualization of a novel oleogel classification to high-, medium-, and low-input methods based on the overall heat, electrical energy consumption, and time input for each oleogel preparation method. EC and LMWGs stand for ethylcellulose and low molecular weight gelators, respectively

proved that a uniform heat dissipation could be achieved, leading to homogeneous gels with consistent physical properties (comparing small and large oleogel batches) [144].

It should be noted that the sustainability and feasibility of oleogelation approaches depend on the commercial availability of the gelators or ingredients that are required in the methods. For example, a semi-direct oleogelation approach may be challenging to be scaled up if the microparticles used in the method are not commercially available or if preparing them requires a high energy input. However, when microparticles are commercially available, this method requires very low

inputs, and therefore can be considered a gentle and sustainable way to produce oleogels at large scale in the food industry. Moreover, various factors beyond the technical aspects of oleogelation must also be taken into account when considering an industrial-scale aim. These factors may include the cost and availability of gelators, as well as the capital and operating costs associated with different oleogelation approaches. The health implications of the gelators, the physicochemical and viscoelastic properties of the resulting oleogels, possible regulatory barriers, and logistics and transportation expenses should also be accounted for when selecting an oleogelation approach [145]. Therefore, a low-input oleogel preparation method will not necessarily lead to an oleogel that can be used in all food applications at any production level. Obtaining an oleogel that is applicable across many food categories still remains a significant challenge. Nonetheless, our novel classification system can potentially help in understanding the effects of different methods on the oxidative stability, sustainability, and industrial viability of the oleogel. It also provides a fresh perspective and tool to facilitate the transition of oleogel preparation from lab to industrial scale.

4.5 Conclusions

In this chapter, oleogel preparation methods developed until early 2023 were reviewed and described giving the reader a full overview of the topic. The development of the oleogel preparation methods was initially inspired by traditional oil structuring techniques and solid fats present in nature. The first methods to be developed were straightforward and intuitive, involving the direct addition of gelators, oil-soluble compounds that can directly structure oil based on solvent–solvent, solvent–particle, and particle–particle interactions. These early works successfully discovered most of the regularly used gelators in the field, establishing the foundation of oleogel research. As the potential of oleogels became apparent, researchers began to explore new methods based on the development of one or more intermediate stages before obtaining an oleogel, including hydrogels, emulsions, foams, aerogels, fibers, and particle dispersions. These efforts have led to breakthroughs aimed at (i) broadening the range of gelators to increase consumer acceptability, (ii) addressing the disadvantages of previous oleogelation methods, and (iii) tailoring oleogel properties envisioning specific applications. In this chapter, a new classification of oleogels based on industrially relevant parameters has also been discussed, in an attempt to bring the benefits of oleogels a step closer to society. The research on oleogels is still ongoing and new methods are expected to emerge in the future.

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