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Additional Information

Review

Recent trends in oil structuring using hydrocolloids

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ABSTRACT

Solid fats provide desirable functionality, texture, and palatability to foods; however, they are related to adverse chronic health effects. Consumers and regulatory authorities are demanding more natural and healthy ingredients. Thus, in context of the high demand for healthy foods and the transition to more sustainable ingredients, oil structuring emerges as an outstanding strategy to substitute saturated and *trans* fats. Researchers have developed optimised indirect routes to structure oil with hydrocolloids resulting in gelled emulsions and oleogels. Novel healthy food structures based on polysaccharides, proteins, and their supramolecular interactions are suitable to create several types of healthy colloidal systems with unique sensory, texture, and stability properties.

1. Introduction

Oils and fats are important to our diet due to being an important energy source and solvent for key nutrients like vitamins and bioactive compounds. In foods, fats provide desirable functionality, texture, and palatability (Pehlivanoğlu et al., 2018). Fats had long been considered a bad influence on health, but, studies have shown that, principally, *trans* and some saturated fats are to blame (Liu et al., 2017; Zhu, Bo, & Liu, 2019). However, saturated fats have a technological role in foods because they are responsible for texture properties (Co & Marangoni, 2018). Solid-like lipids are preferred when processing some industrial products due to their specific features like better oxidative stability and solid lipid functionality. However, widely used methods, such as hydrogenisation, interesterification, and fractionation produce *trans* fatty acids which have severe adverse effects on coronary heart disease, blood lipoprotein profiles, diabetes, and cancer (Pehlivanoğlu et al., 2018). Academy researchers and research development experts have moved toward investigating ways for cheap and healthy production of solid fats with vegetable oil. Still, to replace saturated and *trans* fats in foods, maintaining their physicochemical and sensory properties is still a challenge (Iqbal, Xu, Huang, & Chen, 2019).

In the last decade, considerable progress in oil structuring technology has been made. Semisolid colloidal systems like oleogels incorporate a high percent of liquid oil within a structured network (composed by structurants) to give solid-like properties (Patel, Cludts, Sintang, Lesaffer, & Dewettinck, 2014). Moreover, highly concentrated gelled emulsions such as high internal phase emulsions (HIPEs) have gained popularity in this scientific field. However, an oleogelation limitation is the available food-approved structurants suitable for gelling liquid oils; of which hydrocolloids appear to be the most promising candidate. Generally, the gelling concentrations of hydrocolloids are remarkably low because of their large molecular sizes, making them efficient structuring agents. Still, most food-approved polymers are fundamentally hydrophilic and cannot be dispersed easily in oil to achieve the necessary structure and network formation required for gelation (Patel, 2018; Pernetti, van Malssen, Flöter, & Bot, 2007).

Hydrocolloid-based oleogelation is possible using indirect methods, an innovative solution to structure oil (Martins, Vicente, Cunha, & Cerqueira, 2018). This group includes: i) The emulsion-template approach where the emulsion formation is followed by evaporation of water, giving tightly packed droplets. ii) A solvent exchange procedure replacing the internal aqueous phase with an intermediate solvent followed by liquid oil. iii) The physical sorption of oil in porous structures such as aerogels or cryogels (Nephomnyshy, Rosen-Kligvasser, & Davidovich-Pinhas, 2020). In addition, HIPEs are templates to create oil continuous gels using low-temperature-triggered gelation of closely packed water droplets (Patel and Dewettinck, 2015).

Several types of hydrocolloids can produce novel structures because of their supramolecular interactions. Proteins are amphiphilic molecules that can adsorb strongly at an oil-water interface, thus are highly

effective emulsifiers. Still, the functional properties of proteins can be lost in acidic conditions, at high temperature, high ionic strength, and in organic solvents, limiting their industrial uses (Akhtar & Ding, 2017). Polysaccharides are high-molecule-weight, hydrophilic, and biodegradable polymers regularly used as thickeners to affect the viscosity of aqueous phases to stabilise emulsions. However, many have poorer oil-water interfacial activity than proteins because of the lack of hydrophobic segments (Iqbal et al., 2019). The availability of many food-grade proteins and polysaccharides, and the versatility of the protein-polysaccharide interaction mechanisms, are fundamental to design suitable hydrogels that will later become oleogels (Anal, Shrestha, & Sadiq, 2019). These interactions have countless applications to improve the physical stability of the emulsion systems, and therefore in oleogels stabilisation.

Among indirect methods that require emulsification (such as the emulsion-template approach or HIPE gelation), a new category of food emulsifiers have increased interest from the oleogelation research field. Colloidal solid particles can form strong mechanical interfacial barriers via Pickering emulsions, anchoring at the interface as they can have an affinity for both oil and water (Berton-Carabin & Schroën, 2019). Interfacial layers containing Pickering particles give emulsions high physical stability, essential to develop stable gelled emulsions and oleogels (Lee, Tan, Ravanfar, & Abbaspourrad, 2019; Ma, Zou, McClements, & Liu, 2020).

In this review, the most recent insights of oleogelation using protein and polysaccharides are argued regarding the principal reasons that can influence the interactions and consequently the oleogelation. The promising hydrocolloid-based indirect oil structuration strategies, the development and incorporation of HIPE gels, and using Pickering emulsions with micro- and nanoparticles are discussed. Furthermore, functional colloid formation, current applications, and potential applications of structuring hydrocolloids are discussed.

2. Polysaccharides and proteins as structurants

Oleogelation is achieved by combining a structuring agent (structurant or oleogelator) with liquid oil to confer solid-fat functionality. Oil structuring agents can be classified into two groups based on their molecular weight: low and high molecular weight oil gelators (Co & Marangoni, 2018). High molecular weight oil gelators are mainly proteins and polysaccharides, which can form three-dimensional polymeric networks through physical interactions. Such oleogels have viscoelastic properties which strongly depend on the polymer molecular weight, conformation, and concentration (Davidovich-Pinhas, 2019; Marangoni & Garti, 2011). These polymeric oleogelators can be proteins and polysaccharides or protein-polysaccharide complexes and conjugates (Co & Marangoni, 2018).

2.1. Polysaccharides

Using polysaccharides as structuring agents, stabilisers, or thickening agents in water-based systems is proven in the food industry. They are generally recognised as safe status. Most polysaccharides cannot adsorb at interfaces because of their strong hydrophilic character, however, polysaccharides, like cellulose derivatives, can adsorb as they are surface-active. Because of the hydroxyl groups reactivity on cellulose, many derivatives can be synthesised displaying various physical and chemical characteristics. Ethyl-cellulose, methylcellulose, and hydroxypropylmethyl cellulose (HPMC) are cellulose ethers used in food and other industries. To date, ethyl-cellulose only has the capacity to directly gel liquid oil due to its lipophilic characteristics. Therefore, gelation of oil using polysaccharides is achieved using indirect methods (Davidovich-Pinhas, Barbut, & Marangoni, 2016). Adding methyl and hydroxypropyl groups to cellulose chains give a polymer with a high surface activity. Despite these hydrophobic groups in the cellulose derivative chain, the polymers in part keep the hydrophilic characteristic

of cellulose (Meng, Qi, Guo, Wang, & Liu, 2018b).

Various unique polysaccharides are found in marine organisms like alginates, agar, and carrageenan. Seaweed polysaccharides are favoured among polysaccharides because of their biocompatibility, relatively low cost, and food-grade status. Carrageenan is a family of natural, water-soluble, sulphated galactans isolated from red seaweeds. Carrageenan gelation chains are linked through double helices using cation mediated aggregation to develop a cohesive network. Alginates, obtained from brown seaweeds, can interact with divalent ions forming cross-linking junctions leading to gelation. Hydrogels made of alginate have advantages like high oil retention, lipid oxidation inhibition, lipid digestion control, and target compound's controlled-release. Additional sources of carbohydrates are found in many bacteria species such as xanthan gum. Further, combinations of this hydrocolloid with plant galactomannans like locust bean gum and guar gum give a synergistic viscosity increase (Davidovich-Pinhas, 2019; Lim et al., 2020).

In emulsion-based indirect technologies, combining surface-active and non-surface-active polysaccharides is mandatory to generate stable oleogels containing high liquid oil concentration (Patel, Cludts, et al., 2014). The surface-active polysaccharide can adsorb at the water-oil interface and acts as an emulsifying agent; whereas non-surface-active polysaccharides increase the viscosity of a continuous aqueous phase and act as a thickening agent preventing the coalescence of oil droplets. Addition of non-surface-active polysaccharides is mainly due to three factors: i) an increase in the bulk phase viscosity, ii) interaction with the surface-active component, forming complexes that show a higher interfacial activity, and iii) to anchor to the surface-active component and improve the interfacial stability, due to the cooperation between the two polysaccharides. To obtain the oleogel, selective evaporation of the aqueous phase is conducted, promoting the network formation which results in the entrapment of oil drops in the matrix formed by the combination of both polysaccharides (Meng et al., 2018b; Patel, 2018).

2.2. Proteins

Proteins used as oleogelators to structure oil is difficult, proteins do not easily make networks in oil or hydrophobic environments. Proteins are surface-active materials comprising flexible hydrophobic and hydrophilic moieties. Although proteins are amphiphilic, their hydrophilic attributes limit their oil dispersibility. Therefore, an indirect method is necessary to include proteins in hydrophobic environments (Garti & Benichou, 2004; Scholten, 2019).

Proteins can form protein oleogels, and their properties can be modified by changing the proteins' interactions in the oleogels, also by changing the characteristics of the aqueous phase. This is achieved by reducing the electrostatic repulsion of charged proteins by altering their pH values close to their isoelectric point or by adding salts. Therefore, they come in to such close contact that attractive van der Waals forces dominate. Thus, the repulsive and attractive forces determine the network structure during aggregation (Scholten, 2018).

Alternative electrostatic mechanisms involve heating the protein inducing denaturation, exposing their hydrophobic groups and aggregation to form a three-dimensional network. Protein bonds are strong and when cooled or the aggregates are diluted they do not break. Even covalent bonds may form as disulphide bridges. Protein from different sources can provide disulphide bridges depending on their amino acid's chemical composition (Mehalebi, Nicolai, & Durand, 2008).

Protein-based oleogelation research has been focused on using whey protein. For these proteins, the network formation and how these proteins can be changed, together with how aggregates are made, is well known. However, other proteins may also be suitable for preparing small aggregates as initial building blocks for network formation (Scholten, 2018). Water gelation hydrogels using proteins is common and include milk-derived proteins (de Vries, Wesseling, van der Linden, & Scholten, 2017), gelatin (Zhang et al., 2019), egg proteins (Tang, Yu,

Lu, Fu, & Cai, 2019), and many plant-based proteins (Tavernier, Patel, Van der Meeren, & Dewettinck, 2017; Vélez-Erazo, Bosqui, Rabelo, Kurozawa, & Hubinger, 2020). However, the process of oil structuring is much more challenging.

Increasing global population has led to increased demand for protein which could cause a shortage of protein provision, and a serious future challenge. Current consumer trends have caused the food industry and scientific community to concentrate their efforts on developing oleogels using sustainable techno-functional ingredients sources, such as insect protein-based emulsifiers (Gould & Wolf, 2018) or protein extracts from microalgae species (Ebert, Grossmann, Hinrichs, & Weiss, 2019). These protein sources in oleogel formulations offer a promising innovation for functional fats.

The choice of proteins and suitable methods is determined by the rheological characteristics of the protein oleogels and intended food product. Creating oleogels by adding protein uses two main methods and the protein source used can vary. Using emulsion-template requires a protein that is surface-active. Adding polysaccharides can improve this characteristic by strengthening the interfacial network due to greater attractive interaction with the proteins. With the solvent exchange method, proteins must form aggregates when heating, thus all globular proteins can be used. However, the solvent exchange process gives more control these properties, yet needs an intermediate solvent. Furthermore, disulfide bridges within the protein aggregates give higher stability, slowing their disintegration (de Vries, Lopez Gomez, Jansen, Van der Linden, & Scholten, 2017). These two indirect methods are used to make protein oleogels, however, the preparation has limits for commercial use. Before the proteins can be industrially applied as an efficient oil structuring agent, the limitations must be reduced (Scholten, 2019).

2.3. Protein-polysaccharide complexes and conjugates

Polysaccharides and proteins naturally interact to improve the texture, stability, and quality of food colloidal systems (emulsions, gels, dispersions, foams, and their mixed variants) (Anal et al., 2019; Semenova, 2017).

When these biopolymers are together in a system, their physicochemical properties and interactions are influenced by molar mass, concentration, pH, ionic strength, molecular conformation, charged density, polydispersity, temperature, solvent quality, and nature of interactions (Anal et al., 2019). Proteins and polysaccharide molecules are often connected by either non-covalent interactions (hydrogen bonding, steric exclusion, electrostatic, and hydrophobic) or covalent interaction (enzymatic cross-linking or formation of Maillard reaction products) (Dickinson, 2008).

Non-covalent interactions can be divided into two groups: unlike biopolymers are formed by attraction and repulsion (Fig. 1); these interactions in solution cause complex formations. Attractive electrostatic interactions occur when oppositely charged proteins and polysaccharides come together in the mixed biopolymer system. This leads to soluble or insoluble complexes due to weak or strong interactions, respectively. When the pH is near the protein's isoelectric point, cationic protein's and anionic polysaccharide's interactions form somewhat stable soluble colloidal complexes (Wijaya, Patel, Setiowati, & Van der Meeren, 2017). In contrast, the binding of proteins and polysaccharides with the same amount of opposite charges gives an electrically neutralised insoluble complex and phase separation. Furthermore, the biopolymer-rich phase could aggregate forming a coacervate, depending on the strength of the attraction and nature of the polymers (McClements, 2006). When two polymers with the same charge are mixed, at low ionic strength, there is repulsive electrostatic interaction. Whereas when the biopolymers are at low concentration, they are co-soluble in a single phase. However, when the concentration is above a specific level there is thermodynamic incompatibility and segregate phase separation occurs. Therefore, a two-phase solution results, one rich in a type of biopolymer and depleted in the other, and vice versa (Anal et al., 2019; Rodriguez Patino & Pilosof, 2011).

In contrast, covalent interactions are specific and establish permanent bonds and irreversible interactions between proteins and
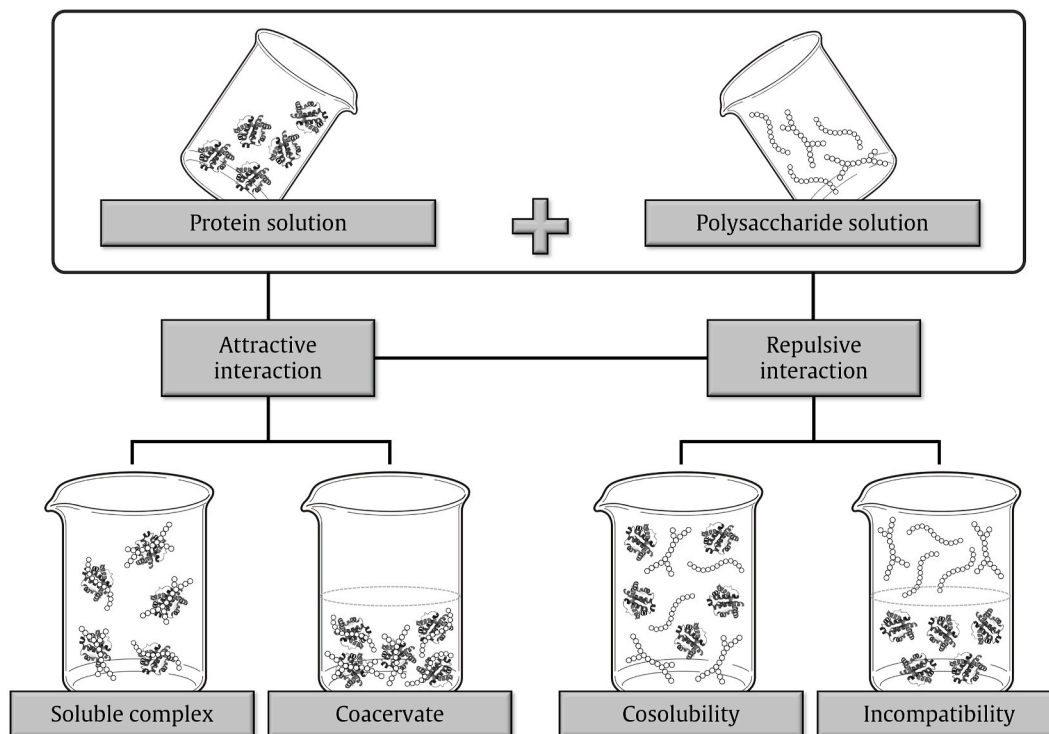

Fig. 1. Schematic representation of the molecular structural arrangements involved when proteins and polysaccharides are mixed together (Adapted from McClements (2006)).

polysaccharides, known as protein glycosylation. This is achieved through a chemical reaction between the protein's amino groups and the polysaccharide's carboxylic groups, resulting in a covalently bound amide (Wijaya et al., 2017). Dehydrating the complex under controlled humidity or by adding a cross-linker, the covalent interaction between proteins and polysaccharides can be induced. Maillard-type conjugates are produced by dry-heating mixtures of two kinds of biopolymers, which improves the protein solubility, colloidal stability, and interfacial functionality (Anal et al., 2019).

The protein-polysaccharide complexes and conjugates show improved functional properties over proteins and polysaccharides alone. This enhancement can be attributed to the biopolymers being both present in the mixture, along with the complexes' structure (Benichou, Aserin, & Garti, 2002).

Protein-polysaccharide interaction mechanisms offer the prospect to design customised colloidal complexes. These combinations have great applications in improving oleogels stabilisation. Different protein-polysaccharide complexes have been formulated to develop hydrocolloids-based oleogels: soy protein-κ-carrageenan (Tavernier et al., 2017), sodium caseinate-xanthan gum, sodium caseinate-guar gum (Abdolmaleki, Alizadeh, Nayebzadeh, Hosseini, & Shahin, 2019), and gelatin-xanthan gum (Abdollahi, Goli, & Soltanizadeh, 2020). Other studies have used protein-polysaccharide conjugates to develop aerogels such as alginate-soy protein (Chen & Zhang, 2020).

2.4. Protein-polysaccharide composite colloidal particles

Some indirect oleogelation methods require an emulsification process such as the emulsion-template approach and HIPE gelation. These methods offer new pathways to improve oleogels stability; one being particle-stabilised emulsions (Berton-Carabin & Schroën, 2015).

Dispersed colloidal particles were found to act as emulsion stabilisers, this concept has been formally recognised since the publication of Pickering (1907) (i.e. Pickering emulsion). The emerging research trends use natural biopolymer particles that act as Pickering stabilisers, which are suitable for food, and can be scaled commercially (Rayner et al., 2014).

Natural biopolymers, like polysaccharides, are a large source of particulate material suitable for food use. Many studies have demonstrated that hydrophobic modified starches, cellulose-based, and chitin-based particles can act as Pickering stabilisers in food-grade emulsions (Dickinson, 2017; Murray, 2019). Additionally, proteins are exceptional natural building blocks for preparing micro- and nanoparticles because of their versatility in tenable conformations (Xiao, Li, & Huang, 2016). The main protein-based particles can be divided by their sources: animal origin (whey protein, bovine lactoglobulin, bovine serum albumin, α-lactalbumin, lactoferrin, and gelatin) and plant origin (prolamins like gliadin from wheat, soy protein, and pea protein). However, plant-based proteins are more relevant for renewable, sustainable, and eco-friendly reasons (Tavernier, Wijaya, Van der Meeren, Dewettinck, & Patel, 2016). Another interesting theoretical approach to produce Pickering emulsifiers uses protein-polysaccharide-based nanoparticles (Xiao et al., 2016).

Innovative opportunities for food emulsion stabilisation using biopolymer nanoparticles and microparticles are transpiring, with stabilisation and durability regarding coalescence, showing no significant changes after long storage periods. This is due to the effective steric structural barrier formed by adsorbed solid particles (Dickinson, 2013; Semenova, 2017). Recently, protein-polysaccharide composite particles are emerging as Pickering stabilisers to develop oleogels such as gliadin-chitosan (Zhou et al., 2019), gliadin-arabic gum (Ma et al., 2020), or bovine serum albumin-cellulose nanocrystals (Liu, Zheng, Huang, Tang, & Ou, 2018). A noteworthy approach is using Pickering emulsions or Pickering HIPEs as templates to give structure to low-viscosity liquid oil forming soft solids and oleogels (Tavernier et al., 2016; Zeng et al., 2017).

3. Indirect methods to structuring liquid oils with hydrocolloids

The most common indirect methods include i) the emulsion-template approach, ii) a solvent exchange procedure, iii) physical sorption of oil into porous structures such as an aerogel or cryogel, and iv) HIPE gelation.

3.1. Emulsion-template approach

The emulsion-template is one of the most progressive multistep processes for oil structuring using indirect methods. This concept was first introduced by Romoscanu and Mezzenga (2006). They prepared a template emulsion with β-lactoglobulin proteins as the emulsifying agent. The process was accomplished by cross-linking adsorbed protein, either thermally or chemically using glutaraldehyde. However, to remove the several washing steps needed to allow protein adsorption at the oil interface, Patel, Cludts, et al. (2014) prepared oleogels by combining food polymers, used as templates, to create oil-based gels with high oil content, without using the cross-linking procedure.

This methodology involves removing the hydrophilic phase in the primary emulsion, then the exposed polymeric structure entraps the oil fraction, forming an oleogel. The polymer forms a hydrophilic solution, and is added to an oil phase with high energy homogenisation (e.g. Ultra-Turrax). After, once dehydration is complete, the exposed biopolymer structure functions as the building block for oleogelation. The oil can intake ≥97% of liquid oil with this technique, as previously demonstrated (Martins et al., 2018).

Several studies used the emulsion-template to develop edible oleogels, using combined surface-active and non-surface-active food polymers (Patel, 2020b, pp. 307–325). Combining the amphiphilic hydrocolloid with a thickening polysaccharide is favourable to stabilise O/W emulsions for preparing oleogels (Rodriguez Patino & Pilosof, 2011). Non-adsorbing hydrocolloids enhance the bulk phase viscosity by forming an extended network, and reinforce the network using adsorbed hydrocolloids molecules at the interfaces of oil droplets (Garti & Leser, 2001; Khouryieh, Puli, Williams, & Aramouni, 2015; Meng, Qi, Guo, Wang, & Liu, 2018a).

Two alternatives where emulsion droplets can be stabilised using protein-polysaccharide complexes exist (Dickinson, 2008). Different authors referred to these two cases as "bilayer emulsions" (method A) and "mixed emulsions" (method B); shown in Fig. 2. Method A comprises making a primary emulsion using protein as the only emulsifier, followed by adding a charged polysaccharide to the aqueous phase, producing a secondary emulsion; thus, giving droplets a protein-polysaccharide 'bilayer' surface coating. Method B requires a bulk aqueous solution of the protein-polysaccharide complex, to be used as the emulsifying agent during a following homogenisation (Jourdain, Leser, Schmitt, Michel, & Dickinson, 2008). Depending on which method is used, emulsions with different textural properties and stability will be obtained.

Different protein-polysaccharide complexes were formulated to develop hydrocolloids-based oleogels using the emulsion-template approach: gelatin-xanthan gum (Patel et al., 2015), soy protein-κ-carrageenan (Tavernier et al., 2017), and sodium caseinate-xanthan gum/guar gum (Abdolmaleki et al., 2019). Other approaches used a combination of surface-active cellulose derivates, such as HPMC or methylcellulose, with the addition of other hydrocolloids, like thickening agents such as carboxymethyl cellulose, xanthan gum, sodium alginate, arabic gum, guar gum, or flaxseed gum (Bascuas, Hernando, Moraga, & Quiles, 2019; Martins et al., 2018; Meng et al., 2018a, 2018b). Another interesting potential application could alter the properties of the emulsion-template oleogel by combining hydrocolloid-based oleogelators (proteins and polysaccharides) with a low concentration of wax. Both alternative oil structuring options were explored by Tavernier, Doan, Van der Meeren, Heyman, and Dewettinck (2018) and Gao and Wu (2019), using soy protein-wax and starch-wax,
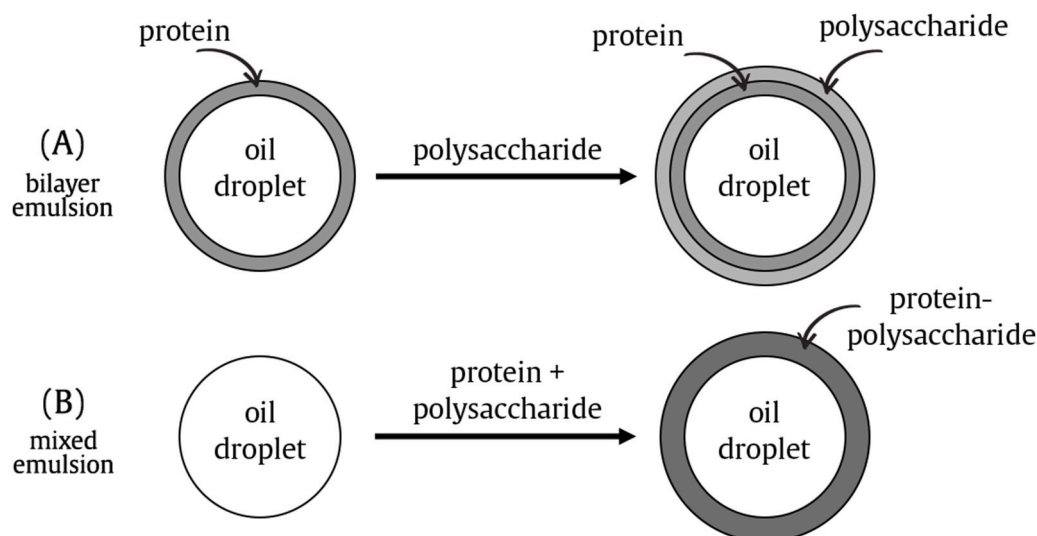
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Fig. 2. Illustration of two procedures for stabilisation of oil droplets using protein-polysaccharide complexes: (A) 'bilayer emulsion' preparation, with polysaccharide added after prior emulsification with a protein; (B) 'mixed emulsion' preparation, with both biopolymers present during emulsification (adapted from Dickinson (2008)).

respectively.

3.2. Solvent exchange

Solvent exchange is an indirect method useable for oleogel development with protein aggregates and polysaccharides as building blocks. Introduced by de Vries, Hendriks, Van Der Linden, and Scholten (2015), the first step of gelation includes developing a hydrogel through producing a polymeric network in an aqueous medium. It has been shown that heat-set whey protein hydrogels can be macroscopic templates and by using the solvent exchange method, can create protein oleogels (de Vries et al., 2017). This method replaces the water in the internal areas of the heat-set protein matrix using an intermediate organic solvent to replace the water content. Subsequently, this will be later replaced with the oil phase via a sequence of immersion steps, responsible for incorporating the oil within the polymeric network (Martins, Vicente, Pastrana, & Cerqueira, 2020).

Intermediate solvent alternatives are limited, however acetone and tetrahydrofuran can fit well (de Vries et al., 2015). The protein network structure remained and was not affected by different solvents. The features of the final protein oleogel are dependant of the protein-building block's properties and their interactions. Therefore, small protein aggregate building blocks result in a spreadable oleogel with plastic behaviour. Whereas a macroscopically large hydrogel leads to a firm oleogel with fracture properties. Because the protein-building blocks are made in an aqueous phase, it is possible to modify the properties of the protein oleogel by changing the setting conditions during the aggregation step (e.g. pH and ionic strength) (Marangoni & Garti, 2011; Scholten, 2018).

The solvent exchange path can be exploited to produce oleogels, even with non-protein hydrocolloids such as κ-carrageenan (Manzocco et al., 2017). The κ-carrageenan hydrogel is first converted into an alcohol-gel using solvent exchange, this is then subjected to supercritical CO_2 drying to give a porous aerogel. This method could be used with other hydrocolloids to create aerogels which absorb a substantial amount of liquid oil (up to 80% capacity) (Patel, 2020a).

3.3. Physical sorption of oil into porous materials

A multitude of challenges have focused on oleogel-derived structures. The drying step is a shortcoming related to the process methods, which is need to remove the aqueous phase and expose the formed gel network. One must achieve oil structuring functionality previous to the hydrocolloid gelation in the water phase. After, the water should be removed, keeping the hydrocolloid structure, guaranteeing successful oil entrapment (Plazzotta, Calligaris, & Manzocco, 2019). A porous structure is produced in the drying process, and can be achieved by using supercritical CO_2 forming aerogels or by freeze-drying, forming cryogels. Besides, aerogels and cryogels have been recognised as tools for bioactive compound microencapsulation in food because of their low density and high porosity properties (Comin, Temelli, & Saldaña, 2012; De Marco, Baldino, Cardea, & Reverchon, 2015).

3.3.1. Aerogels

Aerogels can be defined as a highly porous solid material with low density and high specific surface area. The definition of aerogel is still ambiguous due to its varied physicochemical properties, which depend on the production methods, like the drying procedure. Aerogels could be used with any highly porous solid material with low density, large inner surface area, and high porosity when the liquid in the three-dimensional network is replacing by gas during the preparation process (Zheng, Tian, Ye, Zhou, & Zhao, 2020).

The desire for ecological materials in aerogel fabrication has led focus to turn to biopolymers, believed to be promising precursors. The mechanical robustness and biodegradability of bio-aerogels have remarkable advantages. At present, bio-aerogel investigation is focused on polysaccharides (Obaidat, Alnaief, & Mashaqbeh, 2018; Zhao, Malfait, Guerrero-Alburquerque, Koebel, & Nyström, 2018) and proteins (Ahmadi, Madadlou, & Saboury, 2016; Kleemann, Selmer, Smirnova, & Kulozik, 2018). Some polysaccharides have been fabricated into aerogels successfully, showing excellent properties, including cellulose (Zhang, Zhai, & Turng, 2017), starch (Abhari, Madadlou, & Dini, 2017; De Marco, Riemma, & Iannone, 2019), chitosan (Obaidat, Tashtoush, Bayan, Al Bustami, & Alnaief, 2015), pectin (Tkalec, Knez, & Novak, 2015), and κ-carrageenan (Obaidat et al., 2018). The unique properties of polysaccharide aerogels include biodegradability, biocompatibility, sustainability, and renewability at relatively low cost make them ideal for food use.

As we mentioned in section 3.2, a two-step solvent exchange route to create aerogels then oleogels was exploited by Manzocco et al. (2017) using non-protein hydrocolloids like κ-carrageenan. The hydrogel contained different κ-carrageenan concentrations which were first converted into an alcohol-gel (maintained for 1 day in aqueous solutions of ethanol), followed by an alcohol extraction from the gel using a

supercritical CO_2 drying to obtain a porous aerogel structure (dried template) with larger polymer aggregates. The aerogel showed good capacity to absorb liquid oil (about 80%). However, the oleogels showed a remarkably high firmness and high-volume contraction limiting their food applications. To overcome this issue, Plazzotta et al. (2019) studied the influence of a lettuce-filler addition, derived from fresh-cut lettuce processed in the hydrogel composition, on oleogel structure using κ-carrageenan hydrogel templates, with supercritical CO_2 drying (solvent exchange approach) or freeze-drying (foam template approach).

New approaches could be used with other food-grade hydrocolloids with oil structuring functionality, such as cellulose, marine polysaccharides, or starch (Mikkonen, Parikka, Ghafar, & Tenkanen, 2013) to create oleogels with tailored physical properties using an aerogel template. Recently, Plazzotta, Calligaris, and Manzocco (2020) developed oleogels using a whey protein-based aerogel as a template with freeze-drying or supercritical CO_2 drying techniques. When supercritical CO_2 drying was applied, oleogels, with an oil content of 84.8%, presented a more stable structure and a more interesting plastic and semi-solid texture than freeze-drying oleogels.

Oh, Lee, Lee, and Lee (2019) produced solid-like oleogels from canola oil with foam-structured HPMC, and proved the HPMC oleogel viability as a substitute for animal fat in meat patties. The beef tallow substituted with HPMC oleogels enhanced the quality of the meat patties, by lowering the cooking volume loss and giving a softer texture. In addition, saturated fatty acid levels significantly reduced to 15% compared to the beef tallow sample (42%).

A novel and facile method was reported by Chen and Zhang (2020), using a protein-polysaccharide complex, by cross-linking the alginate-soy protein via the Maillard reaction. Real world applicability should be carefully assessed regarding the long times and dedicated equipment required for creating oleogels by the aerogel template approach. However, characteristics of the aerogels prepared from marine and plant-derivatives polysaccharides have potential for the food industry (Mikkonen et al., 2013).

3.3.2. Cryogels

Another method based on physical sorption of oil into porous material that achieves an oil structuring functionality may be conducted by freeze-drying, forming cryogels. A study by Patel, Schatteman, Lesaffer, and Dewettinck (2013) found, for the first time, an eco-friendly low-temperature system of making oleogels as a different way use a biopolymer to structure oil, referred to as foam template oleogels. They foamed and freeze-dried an HPMC solution to form a porous structure which absorbed a significant volume of oil. The freeze-drying process creates an open cell structure, and under compression oil is released from the oleogel. However, by applying shear to the oil-saturated foams this was prevented by dispersing the polymer sheets and trapping the oil. Because the HPMC foam template oleogels were obtained via shearing, they showed shear stability; thus, are a really good option for spread-like food products.

This relatively facile method using food-grade polymers has been used for practical food applications to decrease saturated fat content in meat patties (Oh et al., 2019), sandwich cookie creams (Tanti, Barbut, & Marangoni, 2016a), muffins (Oh & Lee, 2018), and cakes (Patel & Dewettinck, 2015); they also extended the shelf stable period of peanut butter for over six months (Tanti, Barbut, & Marangoni, 2016b). Therefore, this can generate further research for adapting foam-templates to explore other water-soluble polymers with foaming properties. Recently, Abdollahi et al. (2020) optimised the biopolymers, gelatin and xanthan gum, concentrations to create an oleogel as a freeze-dried foam template. This structure demonstrated an oil binding capacity (>92%) with thixotropic behaviour and 60% structural recovery.

In solid foams, physical properties of cryogels can be defined by their pore size, shape distributions, and the organisation of the pores. Therefore, one must control the porous material's structure. Andrieux,

Medina, Herbst, Berglund, and Stubenrauch (2019) recently tackled this issue using microfluidic-aided foam templating, allowing them to make monodisperse and highly ordered chitosan foams.

3.4. High internal phase emulsion (HIPE) gelation

Complex colloidal systems have become popular in multidisciplinary fields due to a variety of potential applications. This sub-category contains colloidal systems that have an unusual phase distribution such as HIPEs (Wijaya, Van der Meeren, Wijaya, & Patel, 2017). The HIPE's stability plays a key role in their use, when incorporated into products, the stability may affect the product's physicochemical properties and sensory attributes (Liu et al., 2019). HIPEs can form gel-like HIPEs that would have similar properties to oleogels or could be used as the first step of emulsion-template method that requires a production of a stable emulsion to formulate a desirable oleogel (HIPE-template approach) (Fig. 3) (Patel, 2017). HIPE gels stabilised by protein-polysaccharide complexes/conjugates had better coalescence stability than gels stabilised with only proteins or polysaccharides. This was attributed to the greater resistance to rupture by the adsorbed composites (Wijaya, Van der Meeren et al., 2017). However, Pickering HIPE gels, a recent variation of HIPE constituents, are noteworthy as stabilisation is achieved through a layer of rigid particles surrounding each droplet. This leads to greater stability against coalescence, creaming, and Ostwald ripening (Zamani, Malchione, Selig, & Abbaspourrad, 2018) (Fig. 3).
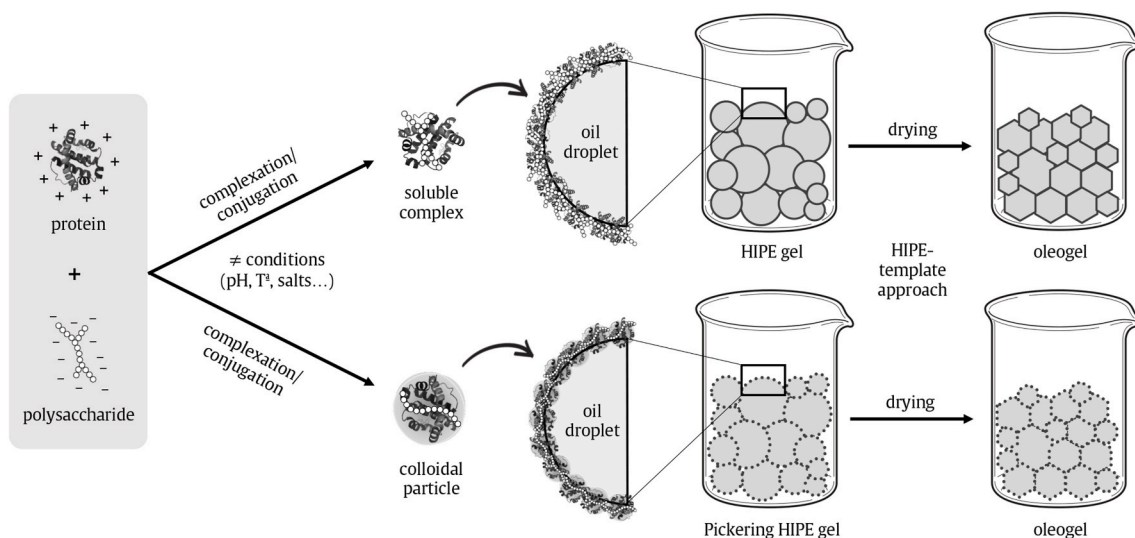
3.4.1. HIPE gels

HIPEs are highly concentrated gelled emulsions with an internal phase volume fraction (Φ) exceeding 0.74 (Cameron & Sherrington, 1996, pp. 163–214). When the internal phase volume fraction is over 0.74, the dispersed droplets achieve their maximum packing density, leading to high viscoelastic flow behaviour. HIPEs' liquid droplets are often squeezed tightly together giving them a polyhedral geometry, and the highest geometric limit for packing of rigid spheres is exceeded (Fig. 3). HIPEs have a highly viscous or gelled soft solid texture (Zamani et al., 2018). Because of these rheological characteristics, HIPEs are popular in numerous applications, such as templates for porous materials (Hori, Sano, Suzuki, & Hanabusa, 2018), foams (Foudazi et al., 2020), oleofilms (Wijaya, Van Der Meeren, Dewettinck, & Patel, 2018), and as enhanced carriers of anti-oxidants (Wijaya et al., 2020).

To date, the modified emulsion-template approach developed by Patel, Rodriguez, et al. (2014) still suffers from long drying times, which can be unfavourable to the oil quality. To circumvent this, HIPEs were used as templates to decrease the overall water content (HIPE-template approach) (Wijaya et al., 2018, 2019). Furthermore, when using HIPE gels, the material that accumulates in the bulk phase decreases the aqueous content giving high oil volume polymer gels or gelled soft solids (Martins et al., 2020; Patel, 2018).

Having control over interfacial properties allows tuning of some gel properties. To achieve high oil content, the droplet surface is stretched to form plateau borders. To prevent droplet coalescence, improving the interface strength, appropriate interfacial proteins can be used. Proteins mostly give a rigid two-dimensional network at the interface, its viscoelastic behaviour with high elasticity make it notable (Nikiforidis & Scholten, 2015). However, high stiffness can stop large deformation, thus can stretch the interface, leading to the interfacial film failure (Van Aken, 2002). Therefore, interfacial layers should have a low dilatational modulus, to allow deformability of the surface, providing a barrier against droplet coalescence. Proteins are excellent emulsifiers as they are amphiphilic, still their stabilisation is improved when mixed with polysaccharides; especially when HIPE gels are formulated (Wijaya, Patel, et al., 2017).

Wijaya et al. (2019) showed how the pH and biopolymer ratio of a sodium caseinate and alginate mixture strongly affected the properties and stability of oleogels made with HIPE templates. Accordingly, in this mixture, the pH played a key role to obtain a highly stable HIPE. In

Fig. 3. Schematic representation of stabilisation procedure of HIPE gels and oleogel formation by protein-polysaccharide soluble complex/conjugate and protein-polysaccharide composite colloidal particle.

addition, the protein to polysaccharide ratio was key to thickening the interface, functioning as a structural framework to entrap the oil phase. Therefore, firmer oleogels with less oil leakage, greater oxidative stability, and stronger gel properties were obtained at a higher polymer mixture ratio (sodium caseinate:alginate; 12:1) with a higher pH (7.0). Besides, Wijaya, Patel, Setiowati, and Van der Meeren (2017) showed that water continuous HIPE gels were successfully prepared, containing an internal phase of 82% and excellent stability, using aqueous dispersions of whey protein isolate-low methoxyl pectin complexes with sunflower oil and homogenising.

Vélez-Erazo et al. (2020) prepared sunflower oil in HIPE using pea protein as an emulsifier, stabilised with multiple polysaccharides (carrageenan, xanthan gum, gum arabic, sodium alginate, pectin, gellan gum, locust bean gum, and tara gum) at a ratio of 4:1. Concerning HIPEs, only the pea protein formulated with xanthan gum and tara gum presented a creamy and homogeneous appearance, with minimal oil loss. Thus, this study provides information to elucidate the interaction behaviour of the pea protein and eight different polysaccharides in structured edible oils. Therefore, can be applicable as fat substitutes in numerous food formulations.

3.4.2. Pickering HIPE gels

Pickering stabilisers, include solid or semisolid particles, can form very stable HIPEs (Zamani et al., 2018) (Fig. 3). Evidence has rapidly accumulated over recent years to indicate gel-like HIPEs can be easily produced using different particles.

Regarding plant proteins, incorporating soy proteins in food is recurrent subject in food colloids, as they are beneficial to health (Tang, 2019). Soy β-conglycinin and soy glycinin, are two key storage globulins in soy protein isolates that could perform as excellent Pickering nanoparticles for stabilising HIPE gels. Hao, Peng, and Tang (2020) showed that untreated soy glycinin exhibited great potential to stabilise HIPE gels. The soy glycinin glycated with soy soluble polysaccharides improved the emulsifying properties of proteins, the gel network stability formation, and the stability against heating or freeze-thawing because of HIPE gels.

Other protein-based particles have been used for HIPE gels stabilisation. Recently, Xu, Tang, Liu, and Liu (2018) stated that native ovalbumin is a remarkable Pickering stabiliser used in O/W HIPE gels, due to its strong intramolecular structural stability, ensuring its particulate nature when adsorbed at an interface. Further, HIPE gels show great coalescence stability upon storage or against heating. Moreover, Xu, Liu, and Tang (2019) demonstrated native soy β-conglycinin, with structural

features like ovalbumin, is also effective as a Pickering nanostabiliser for HIPE gels. The findings are important because of their novel development, eco-friendly, and sustainable HIPEs for food.

Concerning animal protein, Li et al. (2020) confirmed several meat protein particles are excellent emulsifiers to stabilise olive oil in O/W HIPE gels. Stable HIPE gels could be produced at most pH range (pH 3–11) in the continuous phase. In addition, all formed HIPE gels exhibited exceptional stability over 60 days storage, heating, and freeze-thawing.

In contrast, different polysaccharides-derived particles have been used to stabilise HIPE gels. Zhu et al. (2020) prepared stable O/W Pickering HIPEs with chitin nanofibrils as the stabiliser, using a simple two-step strategy. The rod-like chitin nanofibrils gave great stability due to restricting coarsening, droplet breakage, and coalescence when forming the emulsion. Chen et al. (2018) and Chang, Chen, Liu, and Wang (2020) developed Pickering HIPE gels using hydrophobic starch nanocrystals. These nanocrystals were modified by octenyl succinic anhydride (OSA) and were introduced as a stabiliser for gel-like Pickering emulsions. Among all commercial esterification reagents, OSA is the most common and effective to modify starch particles. OSA modification improves starch nanocrystals emulsion ability and offers its use to stabilise Pickering HIPEs (Chang et al., 2020).

Current trends in polysaccharide-based particles have seen use with insoluble fibre-based particles. Phoon & Jeyakumar, 2020 developed a novel approach to create oleogels using only cellulosic fibres, from *nata de coco* and citrus source, to trapped liquid oil in a three-dimensional structure. This study's main finding is that oleogels can be made without oiling off when compressed. Using the fibre source as a gelling agent shows great potential, thus opening the path for using food by-products, such as apple pomace and oat bran, with a high fibre content and bioactive compounds (Huc-Mathis, Journet, Fayolle, & Bosc, 2019).

Yang, Li, and Tang (2020) obtained nanoparticles from the insoluble soy polysaccharides of okara that performed as an outstanding Pickering stabiliser for HIPEs. Okara is a by-product of soybean products, which are rich in polysaccharides and proteins. The findings are of interest to develop novel stable HIPE gels for oil structuring able to incorporate high-added-value use of soybean processing by-products.

Ruan, Yang, Zeng, and Qi (2019) produced a mayonnaise replacer using citrus fibre (soluble and insoluble fibres) and corn peptides (particles) based HIPE gels, with 75% sunflower oil, which increased the dietary fibre in the emulsified food. The resulting HIPE gels showed good heat stability, freeze-thaw recovery, and minimal tribological

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properties; thus, provide more creaminess and smoothness sensory attributes. The citrus fibre-based HIPE gels could provide potential plant-based alternatives with enhanced oral sensation in food application (Yan et al., 2019).

Ma et al. (2020) prepared Pickering HIPE gels using a simple one-step process, blending a gliadin nanoparticle and gum arabic aqueous solution with corn oil (85%). The HIPE gel's apparent viscosity and storage modulus was higher than those stabilised with gliadin nanoparticles alone. Furthermore the authors showed that, the HIPE gels, stabilised by gliadin nanoparticles-gum arabic, formed a dense three-dimensional network, comparatively stable to pH, ionic strength, and temperature changes.

Liu et al. (2018) developed O/W HIPE gels stabilised by bovine serum albumin-covered cellulose nanocrystals by mixing anionic cellulose nanocrystals aqueous solutions with cationic bovine serum albumin at pH 3.0. The surface modification with protein absorption could improve the emulsification performance of cellulose nanocrystals.

Huang et al. (2019) showed that chitosan-caseinophosphopeptides nanocomplexes are effective particulate stabilisers to develop O/W Pickering HIPE gels. A physical barrier was formed on the surface of the oil droplet by the nanocomplexes, and excess of chitosan was dispersed in the continuous phase which formed a network, stabilising the HIPE gels. Furthermore, the Pickering HIPE gels stabilised by the positively charged chitosan-caseinophosphopeptides nanocomplexes were stable after 6 months storage.

Zeng et al. (2017) detailed using gliadin-chitosan hybrid particles as an emulsifier for HIPE gels development. Stable Pickering HIPE gels with internal phases up to 83% were prepared at low particle concentrations. Zhou et al. (2019) fabricated Pickering HIPE gels using gliadin-chitosan complex particles as a stabiliser, the dispersed phase volume fraction (90%) was one of the highest reported food-grade-particle-stabilised Pickering HIPE gels. The particle interfacial barrier and three-dimensional network formed by the complex particles in the continuous phase play key roles in stabilisation of HIPEs and help develop porous materials with a designed pore structure.

4. Conclusions

Under current demands for healthy, natural, and clean-label foods, plus a transition to more eco-friendly and sustainable ingredients, oil structuring using hydrocolloids has emerged as an outstanding strategy to substitute saturated and *trans* fats. Creation of oleogel systems using proteins and polysaccharides profit from hydrocolloid's proven structuring ability in food. However, hydrocolloids used as oil structuring agents raise a challenge due to their hydrophilic nature. Here, we have shown researchers have developed and improved several optimised indirect routes to accomplish such tasks. However, these types of methods can increase the preparation time and complexity leading to a limited industrial application.

Evidence shows HIPEs are being used to form gel-like HIPEs that would have similar final properties as common oleogels. HIPE gels stabilised by protein-polysaccharide complexes and conjugates possess remarkable stability against coalescence, which is attributed to the resistance of the adsorbed complexes and confer unique sensory properties to the systems. Moreover, Pickering HIPE gels show stabilisation is achieved through a layer of rigid particles around each droplet giving extra stability against coalescence, creaming, and Ostwald ripening. Pickering emulsions are a notable item worthy of research in emulsion and colloidal sciences. This has inspired food scientists to use particles as a novel strategy for engineering functional food emulsion interfaces. Physical stability is a benefit, which can relate to the mechanism of stabilisation when compared to conventional emulsifiers. Additional chemical stability, nutritional quality, and controlled delivery benefits also have potential. Innovative food structures owing to oil structuring through hydrocolloids such as oleogels and Pickering HIPE gels are perfect to create several types of colloidal systems with unique and improved properties.

Despite the exponential number of scientific articles published in the field of oil structuring, there is a big gap between scientific research and industrial oleogel preparation. Future research in this field should focus on the development of efficient procedures, reducing time and complexity of the oleogel formation, specifically, at industrial scale. Due to the difficulty of obtaining a good protein-polysaccharide complexation, multidisciplinary approach is expected to be key for future developments.

Moreover, there are some challenges that need to be addressed to enable application of oleogels in food formulations, such as the physical stability or the sensorial properties of the final food products. Development of reformulated products needs to move towards clean and green ingredients to produce healthy and eco-friendly foods, with good acceptability by current and future consumers.

Author statement

Pere Morell: Conceptualization, Writing – original draft, Isabel Hernando: Conceptualization, Writing- Reviewing and Editing, Funding acquisition. Amparo Quiles: Writing- Reviewing and Editing, Funding acquisition, Santiago Bascuas: Writing – original draft

Declaration of competing interest

The authors confirm there are not conflicts of interest.

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References

Abdollahi, M., Goli, S. A. H., & Soltanizadeh, N. (2020). Physicochemical properties of foam-templated oleogel based on gelatin and xanthan gum. *European Journal of Lipid Science and Technology, 122*(2).

Abdolmaleki, K., Alizadeh, L., Nayebzadeh, K., Hosseini, S. M., & Shahin, R. (2019). Oleogel production based on binary and ternary mixtures of sodium caseinate, xanthan gum, and guar gum: Optimization of hydrocolloids concentration and drying method. *Journal of Texture Studies*, (July 2019), 1–10.

Abhari, N., Madadlou, A., & Dini, A. (2017). Structure of starch aerogel as affected by crosslinking and feasibility assessment of the aerogel for an anti-fungal volatile release. *Food Chemistry, 221*, 147–152.

Ahmadi, M., Madadlou, A., & Saboury, A. A. (2016). Whey protein aerogel as blended with cellulose crystalline particles or loaded with fish oil. *Food Chemistry, 196*, 1016–1022.

Akhtar, M., & Ding, R. (2017). Covalently cross-linked proteins & polysaccharides: Formation, characterisation and potential applications. *Current Opinion in Colloid & Interface Science, 28*, 31–36.

Anal, A. K., Shrestha, S., & Sadiq, M. B. (2019). Biopolymeric-based emulsions and their effects during processing, digestibility and bioaccessibility of bioactive compounds in food systems. *Food Hydrocolloids, 87*(August 2018), 691–702.

Andrieux, S., Medina, L., Herbst, M., Berglund, L. A., & Stubenrauch, C. (2019). Monodisperse highly ordered chitosan/cellulose nanocomposite foams. *Composites Part A: Applied Science and Manufacturing, 125*(June), 105516.

Bascuas, S., Hernando, I., Moraga, G., & Quiles, A. (2019). Structure and stability of edible oleogels prepared with different unsaturated oils and hydrocolloids. *International Journal of Food Science and Technology*, 1–10.

Benichou, A., Aserin, A., & Garti, N. (2002). Protein-polysaccharide interactions for stabilization of food emulsions. *Journal of Dispersion Science and Technology, 23*(1–3), 93–123.

Berton-Carabin, C. C., & Schroën, K. (2015). Pickering emulsions for food applications: Background, trends, and challenges. *Annual Review of Food Science and Technology, 6*(1), 263–297.

Berton-Carabin, C., & Schroën, K. (2019). Towards new food emulsions: Designing the interface and beyond. *Current Opinion in Food Science, 27*, 74–81.

Cameron, N. R., & Sherrington, D. C. (1996). High internal phase emulsions (HIPEs) - Structure, properties and use in polymer preparation. In *Biopolymers liquid crystalline polymers phase emulsion*. Berlin, Heidelberg: Springer Berlin Heidelberg.

Chang, S., Chen, X., Liu, S., & Wang, C. (2020). Novel gel-like Pickering emulsions stabilized solely by hydrophobic starch nanocrystals. *International Journal of Biological Macromolecules, 152*, 703–708.

Chen, K., & Zhang, H. (2020). Fabrication of oleogels via a facile method by oil absorption in the aerogel templates of protein-polysaccharide conjugates. *ACS Applied Materials & Interfaces, 12*(6), 7795–7804 (research-article).

Chen, Q. H., Zheng, J., Xu, Y. T., Yin, S. W., Liu, F., & Tang, C. H. (2018). Surface modification improves fabrication of pickering high internal phase emulsions stabilized by cellulose nanocrystals. *Food Hydrocolloids, 75*, 125–130.

Co, E. D., & Marangoni, A. G. (2018). *Oleogels. Edible oleogels*. AOCS Press.

Comin, L. M., Temelli, F., & Saldaña, M. D. A. (2012). Barley beta-glucan aerogels via supercritical CO 2 drying. *Food Research International, 48*(2), 442–448.

Davidovich-Pinhas, M. (2019). Oil structuring using polysaccharides. *Current Opinion in Food Science, 27*, 29–35.

Davidovich-Pinhas, M., Barbut, S., & Marangoni, A. G. (2016). Development, characterization, and utilization of food-grade polymer oleogels. *Annual Review of Food Science and Technology, 7*(1), 65–91.

De Marco, I., Baldino, L., Cardea, S., & Reverchon, E. (2015). Supercritical gel drying for the production of starch aerogels for delivery systems. *Chemical Engineering Transactions, 43*, 307–312.

De Marco, I., Riemma, S., & Iannone, R. (2019). Life cycle assessment of supercritical impregnation: Starch aerogel + Λ-tocopherol tablets. *The Journal of Supercritical Fluids, 143*(September 2018), 305–312.

de Vries, A., Hendriks, J., Van Der Linden, E., & Scholten, E. (2015). Protein oleogels from protein hydrogels via a stepwise solvent exchange route. *Langmuir, 31*(51), 13850–13859.

de Vries, A., Lopez Gomez, Y., Jansen, B., Van der Linden, E., & Scholten, E. (2017). Controlling agglomeration of protein aggregates for structure formation in liquid oil: A sticky business. *ACS Applied Materials and Interfaces, 9*(11), 10136–10147.

de Vries, A., Wesseling, A., van der Linden, E., & Scholten, E. (2017). Protein oleogels from heat-set whey protein aggregates. *Journal of Colloid and Interface Science, 486*, 75–83.

Dickinson, E. (2008). Interfacial structure and stability of food emulsions as affected by protein-polysaccharide interactions. *Soft Matter, 4*(5), 932–942.

Dickinson, E. (2013). Stabilising emulsion-based colloidal structures with mixed food ingredients. *Journal of the Science of Food and Agriculture, 93*(4), 710–721.

Dickinson, E. (2017). Biopolymer-based particles as stabilizing agents for emulsions and foams. *Food Hydrocolloids, 68*, 219–231.

Ebert, S., Grossmann, L., Hinrichs, J., & Weiss, J. (2019). Emulsifying properties of water-soluble proteins extracted from the microalgae: Chlorella sorokiniana and Phaeodactylum tricornutum. *Food and Function, 10*(2), 754–764.

Foudazi, R., Zhao, B., Gokun, P., Manas-zloczower, I., Rowan, S. J., & Feke, D. L. (2020). *The effect of shear on the evolution of morphology in high internal phase emulsions used as templates for structural and functional polymer foams*.

Gao, Y., & Wu, S. (2019). Thermal and oxidation stability of functional oleogels formed by edible wax/starch and Schisandra chinensis oil. *Food and Function, 10*(12), 8056–8068.

Garti, N., & Benichou, A. (2004). Recent developments in double emulsions for food applications. *Food Emulsions, 35*.

Garti, N., & Leser, M. E. (2001). Emulsification properties of hydrocolloids. *Polymers for Advanced Technologies, 12*(1–2), 123–135.

Gould, J., & Wolf, B. (2018). Interfacial and emulsifying properties of mealworm protein at the oil/water interface. *Food Hydrocolloids, 77*, 57–65.

Hao, Z. Z., Peng, X. Q., & Tang, C. H. (2020). Edible pickering high internal phase emulsions stabilized by soy glycinin: Improvement of emulsification performance and pickering stabilization by glycation with soy polysaccharide. *Food Hydrocolloids, 103*.

Hori, K., Sano, M., Suzuki, M., & Hanabusa, K. (2018). Preparation of porous polymer materials using water-in-oil gel emulsions as templates. *Polymer International, 67*(7), 909–916.

Huang, X. N., Zhou, F. Z., Yang, T., Yin, S. W., Tang, C. H., & Yang, X. Q. (2019). Fabrication and characterization of Pickering High Internal Phase Emulsions (HIPEs) stabilized by chitosan-caseinophosphopeptides nanocomplexes as oral delivery vehicles. *Food Hydrocolloids, 93*(February), 34–45.

Huc-Mathis, D., Journet, C., Fayolle, N., & Bosc, V. (2019). Emulsifying properties of food by-products: Valorizing apple pomace and oat bran. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 568*(November 2018), 84–91.

Iqbal, S., Xu, Z., Huang, H., & Chen, X. D. (2019). Structuring of water-in-oil emulsions using controlled aggregation of polysaccharide in aqueous phases. *Journal of Food Engineering, 258*(April), 34–44.

Jourdain, L., Leser, M. E., Schmitt, C., Michel, M., & Dickinson, E. (2008). Stability of emulsions containing sodium caseinate and dextran sulfate: Relationship to complexation in solution. *Food Hydrocolloids, 22*(4), 647–659.

Khouryieh, H., Puli, G., Williams, K., & Aramouni, F. (2015). Effects of xanthan-locust bean gum mixtures on the physicochemical properties and oxidative stability of whey protein stabilised oil-in-water emulsions. *Food Chemistry, 167*, 340–348.

Kleemann, C., Selmer, I., Smirnova, I., & Kulozik, U. (2018). Tailor made protein based aerogel particles from egg white protein, whey protein isolate and sodium caseinate: Influence of the preceding hydrogel characteristics. *Food Hydrocolloids, 83*(May), 365–374.

Lee, M. C., Tan, C., Ravanfar, R., & Abbaspourrad, A. (2019). Ultrastable water-in-oil high internal phase emulsions featuring interfacial and biphasic network stabilization. *ACS Applied Materials and Interfaces, 11*(29), 26433–26441 (research-article).

Li, R., He, Q., Guo, M., Yuan, J., Wu, Y., Wang, S., et al. (2020). Universal and simple method for facile fabrication of sustainable high internal phase emulsions solely

using meat protein particles with various pH values. *Food Hydrocolloids, 100*(October 2019), 105444.

Lim, H. P., Ho, K. W., Surjit Singh, C. K., Ooi, C. W., Tey, B. T., & Chan, E. S. (2020). Pickering emulsion hydrogel as a promising food delivery system: Synergistic effects of chitosan Pickering emulsifier and alginate matrix on hydrogel stability and emulsion delivery. *Food Hydrocolloids, 103*(October 2019), 105659.

Liu, A. G., Ford, N. A., Hu, F. B., Zelman, K. M., Mozaffarian, D., & Kris-Etherton, P. M. (2017). A healthy approach to dietary fats: Understanding the science and taking action to reduce consumer confusion. *Nutrition Journal, 16*(1), 1–15.

Liu, W., Gao, H., McClements, D. J., Zhou, L., Wu, J., & Zou, L. (2019). Stability, rheology, and β-carotene bioaccessibility of high internal phase emulsion gels. *Food Hydrocolloids, 88*(September 2018), 210–217.

Liu, F., Zheng, J., Huang, C. H., Tang, C. H., & Ou, S. Y. (2018). Pickering high internal phase emulsions stabilized by protein-covered cellulose nanocrystals. *Food Hydrocolloids, 82*, 96–105.

Manzocco, L., Valoppi, F., Calligaris, S., Andreatta, F., Spilimbergo, S., & Nicoli, M. C. (2017). Exploitation of κ-carrageenan aerogels as template for edible oleogel preparation. *Food Hydrocolloids, 71*, 68–75.

Marangoni, A. G., & Garti, N. (2011). *Edible oleogels. Edible oleogels*. Urbana, Illnois: First Edit, AOCS Press.

Martins, A. J., Vicente, A. A., Cunha, R. L., & Cerqueira, M. A. (2018). Edible oleogels: An opportunity for fat replacement in foods. *Food and Function, 9*(2), 758–773.

Martins, A. J., Vicente, A. A., Pastrana, L. M., & Cerqueira, M. A. (2020). Oleogels for development of health-promoting food products. *Food Science and Human Wellness, 9*(1), 31–39.

Ma, L., Zou, L., McClements, D. J., & Liu, W. (2020). One-step preparation of high internal phase emulsions using natural edible Pickering stabilizers: Gliadin nanoparticles/gum Arabic. *Food Hydrocolloids, 100*.

McClements, D. J. (2006). Non-covalent interactions between proteins and polysaccharides. *Biotechnology Advances, 24*(6), 621–625.

Mehalebi, S., Nicolai, T., & Durand, D. (2008). The influence of electrostatic interaction on the structure and the shear modulus of heat-set globular protein gels. *Soft Matter, 4*(4), 893–900.

Meng, Z., Qi, K., Guo, Y., Wang, Y., & Liu, Y. (2018a). Effects of thickening agents on the formation and properties of edible oleogels based on hydroxypropyl methyl cellulose. *Food Chemistry, 246*(October 2017), 137–149.

Meng, Z., Qi, K., Guo, Y., Wang, Y., & Liu, Y. (2018b). Macro-micro structure characterization and molecular properties of emulsion-templated polysaccharide oleogels. *Food Hydrocolloids, 77*, 17–29.

Mikkonen, K. S., Parikka, K., Ghafar, A., & Tenkanen, M. (2013). Prospects of polysaccharide aerogels as modern advanced food materials. *Trends in Food Science & Technology, 34*(2), 124–136.

Murray, B. S. (2019). Pickering emulsions for food and drinks. *Current Opinion in Food Science, 27*, 57–63.

Nephomnyshy, I., Rosen-Kligvasser, J., & Davidovich-Pinhas, M. (2020). The development of a direct approach to formulate high oil content zein-based emulsion gels using moderate temperatures. *Food Hydrocolloids, 101*(November 2019), 105528.

Nikiforidis, C. V., & Scholten, E. (2015). High internal phase emulsion gels (HIPE-gels) created through assembly of natural oil bodies. *Food Hydrocolloids, 43*, 283–289.

Obaidat, R. M., Alnaief, M., & Mashaqbeh, H. (2018). Investigation of carrageenan aerogel microparticles as a potential drug carrier. *AAPS PharmSciTech, 19*(5), 2226–2236.

Obaidat, R. M., Tashtoush, B. M., Bayan, M. F., Al Bustami, T., R, & Alnaief, M. (2015). Drying using supercritical fluid technology as a potential method for preparation of chitosan aerogel microparticles. *AAPS PharmSciTech, 16*(4), 1235–1244.

Oh, I. K., & Lee, S. (2018). Utilization of foam structured hydroxypropyl methylcellulose for oleogels and their application as a solid fat replacer in muffins. *Food Hydrocolloids, 77*, 796–802.

Oh, I., Lee, J. H., Lee, H. G., & Lee, S. (2019). Feasibility of hydroxypropyl methylcellulose oleogel as an animal fat replacer for meat patties. *Food Research International, 122*(December 2018), 566–572.

Patel, A. R. (2017). *Edible oil structuring*. Royal Society of Chemistry.

Patel, A. R. (2018). Structuring edible oils with hydrocolloids: Where do we stand? *Food Biophysics, 13*(2), 113–115.

Patel, A. R. (2020a). Chapter 24 - biopolymer-based oleocolloids. In K. Pal, I. Banerjee, P. Sarkar, D. Kim, W.-P. Deng, N. K. Dubey, et al. (Eds.), *587–604*. Elsevier.

Patel, A. R. (2020b). Oil structuring in dairy fat products. In *Dairy fat products and functionality* (pp. 307–325). Springer.

Patel, A. R., Cludts, N., Sintang, M. D. B., Lesaffer, A., & Dewettinck, K. (2014). Edible oleogels based on water soluble food polymers: Preparation, characterization and potential application. *Food and Function, 5*(11), 2833–2841.

Patel, A. R., & Dewettinck, K. (2015). Comparative evaluation of structured oil systems: Shellac oleogel, HPMC oleogel, and HIPE gel. *European Journal of Lipid Science and Technology, 117*(11), 1772–1781.

Patel, A. R., Rajarethinem, P. S., Cludts, N., Lewille, B., De Vos, W. H., Lesaffer, A., et al. (2015). Biopolymer-based structuring of liquid oil into soft solids and oleogels using water-continuous emulsions as templates. *Langmuir, 31*(7), 2065–2073.

Patel, A. R., Rodriguez, Y., Lesaffer, A., & Dewettinck, K. (2014). High internal phase emulsion gels (HIPE-gels) prepared using food-grade components. *RSC Advances, 4*(35), 18136–18140.

Patel, A. R., Schatteman, D., Lesaffer, A., & Dewettinck, K. (2013). A foam-templated approach for fabricating organogels using a water-soluble polymer. *RSC Advances, 3*(45), 22900–22903.

Pehlivanoğlu, H., Demirci, M., Toker, O. S., Konar, N., Karasu, S., & Sagdic, O. (2018). Oleogels, a promising structured oil for decreasing saturated fatty acid

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concentrations: Production and food-based applications. *Critical Reviews in Food Science and Nutrition, 58*(8), 1330–1341.

Pernetti, M., van Malssen, K. F., Flöter, E., & Bot, A. (2007). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science, 12*(4–5), 221–231.

Phoon, P. Y., & Jeyakumar, H. (2020). Fibre-based oleogel: Effect of the structure of insoluble fibre on its physical properties. *Food and Function, 11*, 1349–1436.

Pickering, S. U. (1907). CXCVI.—Emulsions. *Journal of the Chemical Society Transactions, 91*, 2001–2021.

Plazzotta, S., Calligaris, S., & Manzocco, L. (2019). Structure of oleogels from κ-carrageenan templates as affected by supercritical-CO 2 -drying, freeze-drying and lettuce-filler addition. *Food Hydrocolloids, 96*(March), 1–10.

Plazzotta, S., Calligaris, S., & Manzocco, L. (2020). Structural characterization of oleogels from whey protein aerogel particles. *Food Research International, 132*(December 2019), 109099.

Rayner, M., Marku, D., Eriksson, M., Sjöö, M., Dejmek, P., & Wahlgren, M. (2014). Biomass-based particles for the formulation of Pickering type emulsions in food and topical applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 458*(1), 48–62.

Rodríguez Patino, J. M., & Pilosof, A. M. R. (2011). Protein-polysaccharide interactions at fluid interfaces. *Food Hydrocolloids, 25*(8), 1925–1937.

Romoscanu, A. I., & Mezzenga, R. (2006). Emulsion-templated fully reversible protein-in-oil gels. *Langmuir, 22*(18), 7812–7818.

Ruan, Q., Yang, X., Zeng, L., & Qi, J. (2019). Physical and tribological properties of high internal phase emulsions based on citrus fibers and corn peptides. *Food Hydrocolloids, 95*(March), 53–61.

Scholten, E. (2019). Edible oleogels: How suitable are proteins as a structurant? *Current Opinion in Food Science, 27*, 36–42.

Scholten, E. (2018). Chapter 12 - Protein oleogels: network formation of proteins in hydrophobic conditions. In A. G. Marangoni, & N. Garti (Eds.), *Edible Oleogels* (pp. 285–305). AOCS Press.

Semenova, M. (2017). Protein–polysaccharide associative interactions in the design of tailor-made colloidal particles. *Current Opinion in Colloid & Interface Science, 28*, 15–21.

Tang, C. H. (2019). Nanostructured soy proteins: Fabrication and applications as delivery systems for bioactives (a review). *Food Hydrocolloids, 91*, 92–116.

Tang, S., Yu, J., Lu, L., Fu, X., & Cai, Z. (2019). Interfacial and enhanced emulsifying behavior of phosphorylated ovalbumin. *International Journal of Biological Macromolecules, 131*, 293–300.

Tanti, R., Barbut, S., & Marangoni, A. G. (2016a). Hydroxypropyl methylcellulose and methylcellulose structured oil as a replacement for shortening in sandwich cookie creams. *Food Hydrocolloids, 61*, 329–337.

Tanti, R., Barbut, S., & Marangoni, A. G. (2016b). Oil stabilization of natural peanut butter using food grade polymers. *Food Hydrocolloids, 61*, 399–408.

Tavernier, I., Doan, C. D., Van der Meeren, P., Heyman, B., & Dewettinck, K. (2018). The potential of waxes to alter the microstructural properties of emulsion-templated oleogels. *European Journal of Lipid Science and Technology, 120*(3).

Tavernier, I., Patel, A. R., Van der Meeren, P., & Dewettinck, K. (2017). Emulsion-templated liquid oil structuring with soy protein and soy protein: κ-Carrageenan complexes. *Food Hydrocolloids, 65*, 107–120.

Tavernier, I., Wijaya, W., Van der Meeren, P., Dewettinck, K., & Patel, A. R. (2016). Food-grade particles for emulsion stabilization. *Trends in Food Science & Technology, 50*, 159–174.

Tkalec, G., Knez, Ž., & Novak, Z. (2015). Formation of polysaccharide aerogels in ethanol. *RSC Advances, 5*(94), 77362–77371.

Van Aken, G. A. (2002). Flow-induced coalescence in protein-stabilized highly concentrated emulsions. *Langmuir, 18*(7), 2549–2556.

Vélez-Erazo, E. M., Bosqui, K., Rabelo, R. S., Kurozawa, L. E., & Hubinger, M. D. (2020). High internal phase emulsions (HIPE) using pea protein and different polysaccharides as stabilizers. *Food Hydrocolloids, 105*.

Wijaya, W., Patel, A. R., Setiowati, A. D., & Van der Meeren, P. (2017). Functional colloids from proteins and polysaccharides for food applications. *Trends in Food Science & Technology, 68*, 56–69.

Wijaya, W., Sun, Q. Q., Vermeir, L., Dewettinck, K., Patel, A. R., & Van der Meeren, P. (2019). pH and protein to polysaccharide ratio control the structural properties and viscoelastic network of HIPE-templated biopolymeric oleogels. *Food Structure, 21* (March).

Wijaya, W., Van Der Meeren, P., Dewettinck, K., & Patel, A. R. (2018). High internal phase emulsion (HIPE)-templated biopolymeric oleofilms containing an ultra-high concentration of edible liquid oil. *Food and Function, 9*(4), 1993–1997.

Wijaya, W., Van der Meeren, P., Wijaya, C. H., & Patel, A. R. (2017). High internal phase emulsions stabilized solely by whey protein isolate-low methoxyl pectin complexes: Effect of pH and polymer concentration. *Food and Function, 8*(2), 584–594.

Wijaya, W., Zheng, H., Zheng, T., Su, S., Patel, A. R., Van der Meeren, P., et al. (2020). Improved bioaccessibility of polymethoxyflavones loaded into high internal phase emulsions stabilized by biopolymeric complexes: A dynamic digestion study via TNO's gastrointestinal model. *Current Research in Food Science, 2*, 11–19.

Xiao, J., Li, Y., & Huang, Q. (2016). Recent advances on food-grade particles stabilized Pickering emulsions: Fabrication, characterization and research trends. *Trends in Food Science & Technology, 55*, 48–60.

Xu, Y. T., Liu, T. X., & Tang, C. H. (2019). Novel pickering high internal phase emulsion gels stabilized solely by soy β-conglycinin. *Food Hydrocolloids, 88*, 21–30.

Xu, Y. T., Tang, C. H., Liu, T. X., & Liu, R. (2018). Ovalbumin as an outstanding pickering nanostabilizer for high internal phase emulsions. *Journal of Agricultural and Food Chemistry, 66*(33), 8795–8804.

Yang, T., Li, X. T., & Tang, C. H. (2020). Novel edible pickering high-internal-phase-emulsion gels efficiently stabilized by unique polysaccharide-protein hybrid nanoparticles from Okara. *Food Hydrocolloids, 98*.

Yan, C., McClements, D. J., Zhu, Y., Zou, L., Zhou, W., & Liu, W. (2019). Fabrication of OSA starch/chitosan polysaccharide-based high internal phase emulsion via altering interfacial behaviors. *Journal of Agricultural and Food Chemistry, 67*(39), 10937–10946.

Zamani, S., Malchione, N., Selig, M. J., & Abbaspourrad, A. (2018). Formation of shelf stable Pickering high internal phase emulsions (HIPE) through the inclusion of whey protein microgels. *Food and Function, 9*(2), 982–990.

Zeng, T., Wu, Z. ling, Zhu, J. Y., Yin, S. W., Tang, C. H., Wu, L. Y., et al. (2017). Development of antioxidant Pickering high internal phase emulsions (HIPEs) stabilized by protein/polysaccharide hybrid particles as potential alternative for PHOs. *Food Chemistry, 231*, 122–130.

Zhang, C., Li, Y., Wang, P., Zhang, A., Feng, F., & Zhang, H. (2019). Electrospinning of bilayer emulsions: The role of gum Arabic as a coating layer in the gelatin-stabilized emulsions. *Food Hydrocolloids, 94*(February), 38–47.

Zhang, C., Zhai, T., & Turng, L. S. (2017). Aerogel microspheres based on cellulose nanofibrils as potential cell culture scaffolds. *Cellulose, 24*(7), 2791–2799.

Zhao, S., Malfait, W. J., Guerrero-Alburquerque, N., Koebel, M. M., & Nyström, G. (2018). Biopolymer aerogels and foams: Chemistry, properties, and applications. *Angewandte Chemie International Edition, 57*(26), 7580–7608.

Zheng, Q., Tian, Y., Ye, F., Zhou, Y., & Zhao, G. (2020). Fabrication and application of starch-based aerogel: Technical strategies. *Trends in Food Science & Technology, 99* (July 2019), 608–620.

Zhou, F. Z., Yu, X. H., Zeng, T., Yin, S. W., Tang, C. H., & Yang, X. Q. (2019). Fabrication and characterization of novel water-insoluble protein porous materials derived from pickering high internal-phase emulsions stabilized by gliadin-chitosan-complex particles. *Journal of Agricultural and Food Chemistry, 67*(12), 3423–3431.

Zhu, Y., Bo, Y., & Liu, Y. (2019). Dietary total fat, fatty acids intake, and risk of cardiovascular disease: A dose-response meta-analysis of cohort studies. *Lipids in Health and Disease, 18*(1), 1–14.

Zhu, Y., Huan, S., Bai, L., Ketola, A., Shi, X., Zhang, X., et al. (2020). High internal phase oil-in-water pickering emulsions stabilized by chitin nanofibrils: 3D structuring and solid foam. *ACS Applied Materials and Interfaces, 12*(9), 11240–11251.