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Recent Innovations in Emulsion Science and Technology for Food Applications

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ABSTRACT

Emulsion technology has been utilized for decades in the food industry to create a diverse range of products, including homogenized milk, creams, dips, dressings, sauces, desserts, and toppings. Recently, however, there have been important advances in emulsion science that are leading to new approaches to improving food quality and functionality. This article provides an overview of a number of these advanced emulsion technologies, including Pickering emulsions, high internal phase emulsions (HIPEs), nanoemulsions, and multiple emulsions. Pickering emulsions are stabilized by particle-based emulsifiers, which may be synthetic or natural, rather than conventional molecular emulsifiers. HIPEs are emulsions where the concentration of the disperse phase exceeds the close packing limit (usually > 74%), which leads to novel textural properties and high resistance to gravitational separation. Nanoemulsions contain very small droplets (typically d < 200 nm), which leads to useful functional attributes, such as high optical clarity, resistance to gravitational separation and aggregation, rapid digestion, and high bioavailability. Multiple emulsions contain droplets that have smaller immiscible droplets inside them, which can be used for reduced calorie, encapsulation, and delivery purposes. This new generation of advanced emulsions may lead to food and beverage products with improved quality, health, and sustainability.

Keywords: nanoemulsions; nanotechnology; multiple emulsions; Pickering emulsions; HIPEs

INTRODUCTION

Traditional emulsion technology has been widely applied in the food industry to create a diverse range of products, including homogenized milk, cream, dips, dressings, sauces, desserts, and toppings. This technology can also be used to create delivery systems to encapsulate and protect bioactive components, as well as to control their release and enhance their bioavailability.[1-2] Recently, however, there have been a number of advances in emulsion technology that may extend their range of applications within foods.[3] Driven by academic, industrial, and government scientists, a number of novel emulsion types have been developed that may be suitable for food applications, including Pickering emulsions, high internal phase emulsions (HIPEs), nanoemulsions, and multiple emulsions.

These different kinds of advanced emulsions can all be formulated from edible oils, water, stabilizers and additives, however, their potential applications within foods are dependent on their specific compositions and structures. For instance, Pickering emulsions, which utilize colloidal particles rather than molecules as emulsifiers,[4] have strong resistance to droplet coalescence, which may be useful for the creation of emulsified foods where the oil droplets are packed closely together for long periods (such as dressings) or for food products that are frozen and thawed (such as microwave meals) [5]. HIPEs are a specialized type of emulsified system where the concentration of the disperse phase is very high (> 74%), which leads to semi-solid textural properties, a high resistance to gravitational separation, and a high loading capacity.[6] They may therefore be useful in emulsified foods that should be highly viscous or semi-solid, such as dressings, sauces and desserts, or in applications where a large amount of a bioactive component must be encapsulated.[7] The ability of HIPEs to flow at high shear rates but set at low shear rates also makes them suitable for application as edible inks in 3D food printing.[8] The extremely small dimensions of the droplets in nanoemulsions provide advantages for certain food applications, such as improved resistance to droplet aggregation and creaming, enhanced optical clarity, and increased bioavailability of encapsulated substances.[9] Finally, the fact that multiple emulsions, such as water-in-oil-in-water (W/O/W) emulsions, have two different hydrophilic domains within the same system provides advantages for some applications.[10] For instance, two hydrophilic substances that normally react with each other can be isolated from one another, or a bitter tasting hydrophilic substance can be trapped in the internal phase, thereby reducing its sensory perception during mastication. Thus, different kinds of advanced emulsion technologies have different advantages and disadvantages for specific applications in foods.[11] Consequently, food formulators should have knowledge about the formation, stability, properties, and functionality of these different kinds of advanced emulsion technologies so they can choose the most suitable one for a specific application.

In this article, we review the formulation, fabrication, stabilization, and potential food applications of each type of advanced emulsion technology. Moreover, the advantages and disadvantages of the different kinds of these emulsions are discussed, as well as areas where future research is still needed. For the sake of clarity, only oil-in-water type emulsions are discussed because these are the most widely used in commercial foods at present.

PICKERING EMULSIONS

Pickering mechanism and formation

The droplets in Pickering emulsions are coated by colloidal particles instead of molecular emulsifiers.[5] The colloidal particles used for this purpose should have an affinity for both the oil and water phases, so they have appropriate wetting properties. Indeed, particle wettability is a key factor determining the successful formation and stability of Pickering emulsions, which is determined by the contact angle (θ) of a colloidal particle at an oil-water interface,[12] as illustrated in Figure 1a.

Hydrophilic particles ($\theta < 90°$) predominantly protrude into the aqueous phase, which favors the formation of oil-in-water (O/W) emulsions (Figure 1a, upper panel). Conversely, hydrophobic particles ($\theta > 90°$) predominantly protrude into the oil phase, which favors the formation of water-in-oil (W/O) emulsions (Figure 1a, lower panel). Particles that are equally wetter by both phases ($\theta = 90°$) possess the maximum desorption energy (ΔE):[12]

$$\Delta E = \pi r^2 \gamma (1 - |\cos\theta|)$$

Here, r is the colloidal particle radius (nm) and γ is the oil-water interfacial tension (N/m). When the particles have a suitable wettability, the desorption energy is considerably higher than the thermal energy (k_BT). As a result, Pickering emulsions typically have strong resistance to coalescence because the colloidal particles are almost irreversibly attached to the surfaces of the droplets (Figure 1b) and create a mechanically robust particle coating that generates a strong steric repulsion.[13] As a consequence, Pickering emulsions are typically much more stable to coalescence than conventional emulsions.[5] This feature makes them suitable candidates for the generation of emulsion-based foods with enhanced quality attributes and shelf-lives.

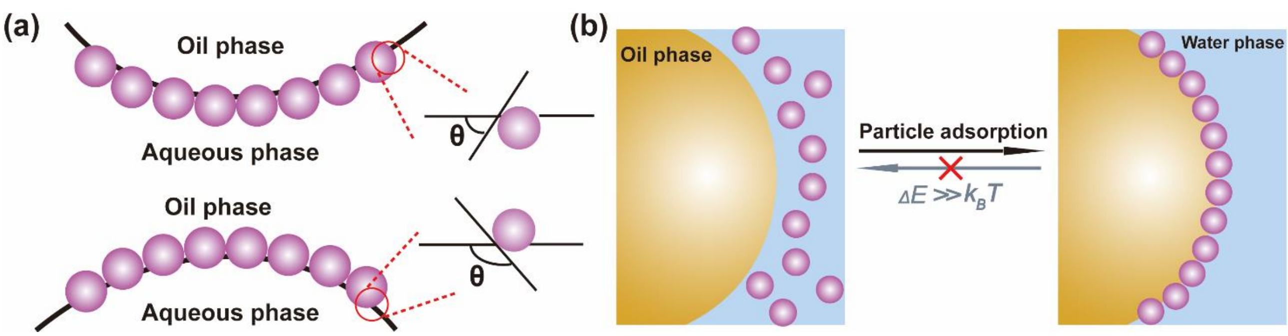

Figure 1. (a) Possible positioning and contact angle of spherical particles at the oil-water interface. Reproduced from ref.13.[12] Copyright 2002 American Chemical Society. (b) Schematic illustration of the adsorption of spherical particles at the water-oil interface with a contact angle smaller than 90°, towards O/W Pickering emulsion.

The fact that such a large desorption energy is needed to detach colloidal particles from droplet surfaces is also important during the formation of Pickering emulsions. Typically, the high energy barrier associated with particle desorption must be exceeded by the application of external forces or by altering solution conditions.[14] Many studies have shown that the intense mechanical forces generated during homogenization helps to overcome this energy barrier,[15-17] allowing the formation of Pickering emulsions containing relatively small droplets. However, if the mechanical forces used are too intense or applied for too long, then the structure of a Pickering emulsion may be disrupted, resulting in a high polydispersity.[18] Therefore, the selection of a proper homogenization method and operating conditions is crucial for the production of Pickering emulsions, as well as for the precise control of their functional properties.

Food-grade stabilizers

Many of the original studies on Pickering emulsions used synthetic colloidal particles that were not appropriate for formulating foods. More recently, however, researchers have shown that a variety of food ingredients can be successfully be used to formulate Pickering emulsions, which may be either inorganic or organic particles.[19] A number of food-grade colloidal particles that have been used for this purpose are reviewed in this section and summarized in Table S1 (Supplementary information).

Inorganic particles. Silica particles have been widely studied for the formation and stabilization of Pickering emulsions.[20] This type of inorganic colloidal particle is an accepted food ingredient,[21] which can therefore be used in formulating food-grade Pickering emulsions.[22-23] Other kinds of food-grade inorganic particles can also be used for this purpose, including those formed from calcium carbonate and titanium dioxide.[24-25] The commercial availability and consistent properties of these inorganic particles make them highly suitable for the formation of food-grade Pickering emulsions. However, the appearance of inorganic particles on food product ingredient labels is often perceived negatively by consumers,[5] which restricts their commercial implementation.

Carbohydrate-derived particles. Carbohydrate-derived particles, such as those assembled from starch, cellulose, and chitin, have been widely explored as food-grade Pickering stabilizers because they can often be obtained from renewable and abundant natural resources.[26] Starch is widely found in tubers and cereals. Starch granules themselves, or smaller colloidal particles derived by controlled disintegration of them, can be used to form Pickering emulsions.[27] Starch particles can also be chemically modified using octenyl succinic anhydride (OSA),[28-30] which increases their hydrophobicity and allows their wetting characteristics to be tailored for specific applications. The hydrophobic octenyl group increases the affinity of the starch particles for the oil phase, which promotes the formation and stabilization of oil-in-water Pickering emulsions (Figure 2a).

Chitin is a polysaccharide isolated from the hard shells of crustaceans, where it is present as tightly bonded microfibrils consisting of extended linear molecular chains of acetylglucosamine homopolymers with varying amounts of primary amines on their surfaces.[31] Chitin nanoparticles can be extracted from chitin using different approaches: (i) *acid hydrolysis*,[32] which results in highly ordered, rigid rod-like chitin nanocrystals (ChNC); (ii) *mechanical shearing*,[33] which results in longer, more flexible chitin nanofibers (ChNF) that retain disordered domains within their structure. Both types of these chitin nanoparticles can be used to successfully prepare food-grade O/W Pickering emulsions, but ChNF appears to be better than ChNC for this purpose.[34-36] This difference may be due to increased surface coverage of the oil droplets, as well as an increase in network formation in the continuous phase (Figure 2b).[37] Unlike chitin, the solubility of chitosan in water is pH-dependent, which results in the formation of chitosan particles under relatively high pH conditions.[38] The ability of chitosan particles to facilitate the formation and improve the stability of food-grade Pickering emulsions has also been demonstrated.[39]

Cellulose, the most abundant biopolymer on Earth, is a fibrous, robust, water-insoluble substance that is the main load-bearing component found in plant cell walls.[40-41] Controlled deconstruction of cellulose-rich fibrous structures in plants, either by chemical or mechanical treatments, can be used to extract two types of cellulosic nanoparticles: cellulose nanocrystals (CNC) and nanofibrils (CNF). Some bacteria are also able to directly produce cellulosic microfibrils that are recognized as bacterial nanocellulose (BNC). These three types of nanocellulosic particles have been comprehensively investigated for their potential to form food-grade Pickering emulsions,[42-45] particularly CNC (Figures 2c and 2d). One of the main limitations of nanocellulose-based Pickering emulsions is the fact that the oil droplets generated are relatively large, which makes them susceptible to creaming during storage. A series of approaches have therefore been developed to reduce the droplet size in nanocellulose-stabilized Pickering emulsions.[46-48] For instance, combinations of different nanocelluloses (CNC and CNF) have been used create Pickering emulsion with extremely good physical stabilities.[49] The adsorbed CNC formed a protective coating around the oil droplets, while the non-adsorbed CNF induced the formation of a droplet network throughout the emulsion through a depletion mechanism. Surprisingly, at a proper CNC-to-CNF ratio, the Pickering emulsions formed were stable for over 6 months without any sign of instability, which may be useful for increasing the shelf life of some food products.

Protein-based particles. Proteins are amphiphilic biopolymers that are widely used as molecular emulsifiers in the food industry. However, various kinds of protein-based colloidal particles can also be used to produce Pickering emulsions, such as protein particles or microgels.[19, 50] The interior of protein particles consists of tightly packed protein molecules with a relatively low amount of water, whereas that of protein microgels consists of an open network of aggregated protein molecules that contains a relatively high amount of water.

Protein particles and microgels can be formed from animal-derived proteins using various methods, including controlled heating, sonication, high-pressure treatment, and pH adjustment. For example, whey protein microgels have been produced by sonicating a protein dispersion at pH 6.5, which resulted in the formation of microgels with an average diameter of around 235 nm.[51] These microgels were successfully used to form oil-in-water emulsions that exhibited good long-term stability. Whey protein microgels fabricated using high hydrostatic pressure treatment have also been used to produce Pickering emulsions.[52] Colloidal protein particles have been produced by heating solutions of globular proteins above their thermal denaturation temperature using carefully controlled ionic strength and pH conditions to promote protein unfolding and assembly into small particles.[53] As an example, Pickering emulsions have been formed from lactoferrin particles produced using this approach.[54-55] More recently, ovotransferrin fibrils formed by controlled heating have also been used for this purpose (Figure 2e).[56]

Colloidal protein microgels or particles derived from plant sources may also be utilized to create and stabilize Pickering emulsions, which is important since many consumers are switching from omnivore to flexitarian, vegetarian, or vegan diets.[57] Many of the approaches used to produce particles or microgels from animal proteins can also be used to produce them from plant proteins. However, some additional methods are also suitable for certain kinds of plant proteins. For example, zein is a hydrophobic protein derived from corn that has poor solubility in water but good solubility in concentrated ethanol solutions. The poor water-solubility of zein allows the fabrication of colloidal protein particles through antisolvent precipitation.[58] Indeed, a recent study showed that zein nanoparticles could be used to form stable Pickering emulsions with oil droplet diameters ranging from 10 to 200 μm.[59] A method that involved controlled heating and then transglutaminase treatment of peanut proteins was recently developed to generate plant protein particles.[60] Soy protein particles formed by heating a protein solution under controlled ionic conditions have been used to produce stable Pickering emulsions (Figure 2f).[61] Similarly, pea protein nanoparticles produced using controlled pH adjustment have also been used.[62] Recently, pea protein particles prepared by controlled shearing of a heat-set gel were also used to form stable Pickering emulsions.[63]

Other particles. A number of other food-grade substances can form colloidal particles that can facilitate the formation and stability of Pickering emulsions. Flavonoids are secondary metabolites from plants, and exist as insoluble particles in aqueous solutions that can adsorb to oil-water interfaces in emulsions.[5] Indeed, flavonoids have been successfully used to produce Pickering emulsions.[64] Shellac wax is a natural edible wax that can be used in foods. It can be converted into colloidal wax particles using antisolvent precipitation under high shear conditions.[65] Shellac-based particles combined with xanthan gum have been shown to form stable Pickering emulsions.[66] Colloidal particles have also been produced from phytosterols and whey proteins using the antisolvent precipitation method.[67] These particles formed platelet-like sheets whose ability to form and stabilize Pickering emulsions depended on the particle concentration and oil fraction used.

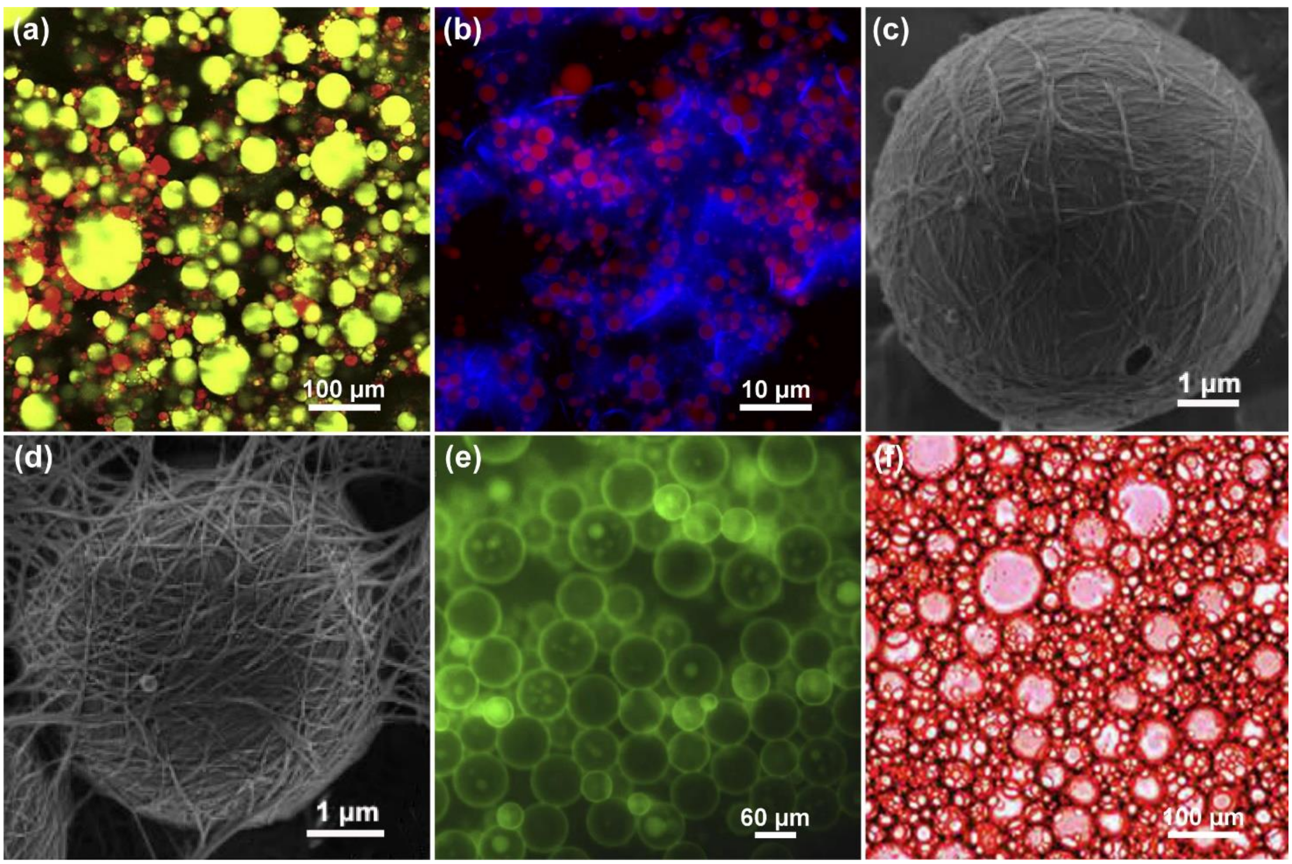

Figure 2. Examples of microscopic images of O/W Pickering emulsions that are stabilized by food-grade particles. (a) Starch particles. Reproduced from ref. 30.[29] Copyright 2011 Elsevier. (b) Chitin nanofibers. Reproduced from ref.38.[37] Copyright 2019 American Chemical Society. Rodlike Cellulose nanocrystals with (c) short and (d) long rod length. Reproduced from ref.69.[68] Copyright 2013 Royal Society of Chemistry. (e) Ovotransferrin fibrils. Reproduced from ref.57.[56] Copyright 2019 Elsevier. (f) Soy protein particles. Reproduced from ref.62.[61] Copyright 2013 American Chemical Society.

Novel applications in foods

In this section, potential applications of Pickering emulsions within the food industry are discussed.

Delivery of active ingredients. Many minor substances found in foods, including vitamins and nutraceuticals, may have beneficial effects on human health but their use is currently limited by their low solubility, chemical stability, and/or bioavailability. Emulsion technology has been widely used to encapsulate these bioactive ingredients so as to protect them from degradation, improve their bioavailability, and control their release profiles.[69] Compared to conventional emulsifier-based emulsions, Pickering emulsions can provide some novel or improved functions due to their unique properties.

Curcumin-loaded Pickering emulsions stabilized by ovotransferrin fibrils were shown to have better environmental stability and bioaccessibility than curcumin dissolved in bulk oil.[70] Similarly, curcumin-loaded Pickering emulsions stabilized by whey protein particles were shown to have enhanced thermal stability.[71] Pickering emulsions stabilized by CNC have been used to encapsulate natural antimicrobial oils (oregano oil).[72] These emulsions were shown to efficiently inhibit the growth of four tested food-related microorganisms by destroying the integrity of the microbial cell walls. In a similar study, thymol was loaded into zein/gum arabic particle-stabilized Pickering emulsions, which were also shown to be effective antimicrobial delivery systems.[73] These emulsions could also be designed to control the release of thymol, which may be beneficial in some situations.

In certain food applications, it is desirable to have delivery systems with controlled or targeted release functions. Based on the pH-responsiveness of chitosan particles, a reversible chitosan particle-stabilized Pickering emulsion was developed whose release properties could be manipulated by lowering the pH.[38] This type of pH-responsive behavior could be used for the release of bioactive compounds in the stomach. Nanocellulose-stabilized Pickering emulsions has been developed to achieve targeted delivery of short-chain fatty acids after intestinal digestion.[74] CNF-stabilized Pickering emulsions have been developed to encapsulate and release vitamin D_3.[75] A high portion of the vitamin remained inside the lipid droplets after intestinal digestion because the CNF formed a protective coating around the oil droplets, which may be useful for delivering the vitamin to the distal regions of the small intestine or to the colon.

Control of lipid digestion. Researchers are developing strategies to control lipid digestion so as to avoid metabolic or hormonal dysregulation. Food-grade Pickering emulsions have recently been investigated for their ability to regulate lipid digestion. For instance, the *in vitro* digestion of CNC-stabilized Pickering emulsions has been compared to the digestion of conventional gum arabic-stabilized emulsions.[76] The final amount of free fatty acids released was around 40% less for the CNC-coated lipid droplets than the gum arabic-coated ones. These results suggest that forming a CNC coating around the oil droplets inhibited lipase adsorption and therefore lipid digestion. In another study, the uptake of digested CNC-stabilized Pickering emulsions by murine intestinal mucosa was evaluated.[77] This study showed that the CNCs were trapped within the intestinal mucus layer and failed to reach the underlying epithelium, which may reduce lipid absorption. In another study, Pickering emulsions stabilized by composite particles containing whey protein and CNC were also shown to inhibit lipid digestion (Figure 3a).[78]

Chitin nanoparticle-stabilized Pickering emulsions have also been shown to reduce lipid digestion using an *in vitro* human gastrointestinal tract (GIT) model.[79] Another recent study using a similar system showed that the bioaccessibility of vitamin D_3 was also reduced.[80] The ability of chitin nanoparticles to reduce lipid digestion and vitamin bioaccessibility may be the result of various processes (Figure 3b): (1) the chitin nanoparticle coating hindered the ability of lipase to reach the lipid phase; (2) the presence of the chitin nanoparticles promoted droplet aggregation in the GIT, thereby reducing the area of lipids accessible to the lipase; and (3) the cationic chitin nanoparticles bound to anionic bile acids, fatty acids, or lipase, thereby interfering with lipid digestion and vitamin solubilization. This study suggested that chitin nanoparticle-stabilized Pickering emulsions may be useful for developing high-satiety foods and for targeted delivery systems.

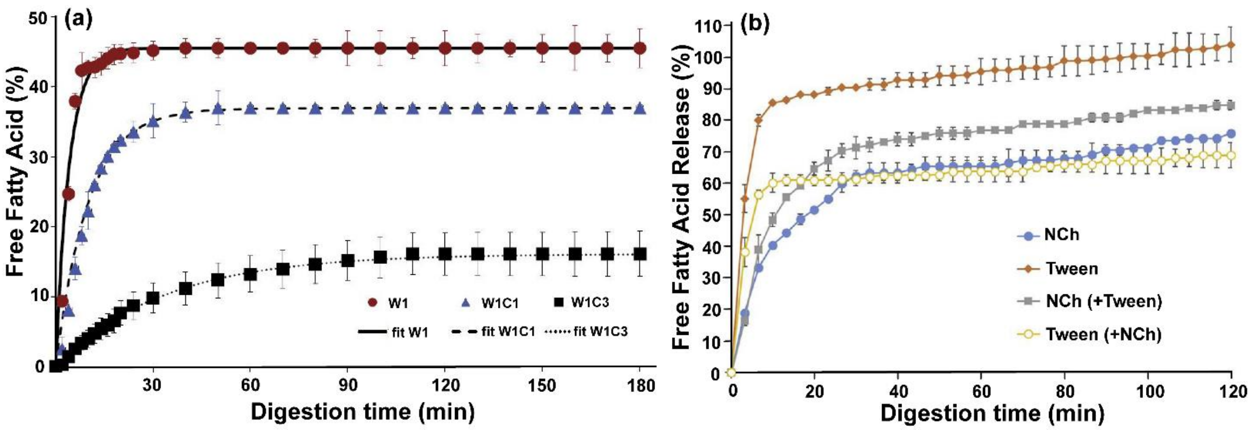

Figure 3. (a) Free fatty acid release of Pickering emulsions formed using different whey protein/CNC composite particles. The whey protein concentration in W1, W1C1 and W1C3 was 1 wt%, and the CNC concentration was 0, 1, and 3 wt%, respectively. Reproduced from ref.79.[78] Copyright 2018 Elsevier. (b) Impact of emulsion type on free fatty acid release under simulated small intestinal conditions. The concentrations for stabilizers upon digestion were identical. Reproduced from ref.81.[80] Copyright 2020 Elsevier.

Inhibition of lipid oxidation. Lipid oxidation is a major problem in foods containing unsaturated lipids because it leads to rancidity. A major cause of the oxidation of lipids in emulsified foods is the tendency for lipid hydroperoxides located at the surfaces of oil droplets to interact with transition metal ions in the surrounding water.[81] Pickering emulsions may be used to improve the oxidative stability of emulsified oils because the thick particle coating formed surrounding the droplets limits the direct contact of the transition metals and lipid hydroperoxides. In addition, some substances used to form Pickering particles, such as proteins, polysaccharides and polyphenols, have inherent antioxidant properties.[82] Studies have shown that the oxidation of emulsified sunflower oil can be inhibited by coating the oil droplets with cellulose nanoparticles, which was presumably because these particles could scavenge free radicals present at the oil droplet surfaces, as well as create a steric barrier around the oil droplets that inhibited interactions between lipids and pro-oxidants.[83] The presence of a layer of protein particles around the surfaces of the oil droplets in Pickering emulsions has also been reported to protect the lipids from oxidation.[84] The antioxidant activity of protein particles is likely to depend on the type, number, and location of the different kinds of amino acid present. For example, cysteine and methionine groups exposed at the surfaces of protein particles could be effective at scavenging free radicals or chelating metal ions, which would effectively inhibit oxidation.[5] In a recent study, Pickering emulsions formulated using gliadin/chitosan nanoparticles as stabilizers were reported to be more resistant to lipid oxidation under conditions where the solution pH was less than the isoelectric point of gliadin.[85] Under these conditions the protein nanoparticles have a high positive charge and so can repel positively charged transition metal ions away from the surfaces of the oil droplets. In summary, previous research suggests that the oxidative stability of emulsified lipids may be improved by coating them with some kinds of particle-based emulsifiers.

Current and future perspectives

In this section, the benefits and limitations of using Pickering emulsions for food applications are discussed, as well as possible future research directions. As mentioned earlier, Pickering emulsions tend to be much more resistance to droplet coalescence than conventional emulsions.[4] This attribute is an advantage in food products containing relatively large oil droplets that are in close proximity for extended periods, such as salad dressings and mayonnaise. Moreover, it may be advantageous in products that have to be resistant to freeze-thaw cycling, such as frozen foods or microwave meals. Pickering emulsions can be prepared from a diverse range of plant-based colloidal particles,[87-88] which is beneficial for the development of plant-based food products.[89] However, there are also a number of potential limitations associated with the utilization of Pickering emulsions within foods. There are some concerns about the potential toxicity of certain kinds of nanoparticles in foods, which may limit their use as emulsifiers to formulate Pickering emulsions.[90] Consequently, more research on the gastrointestinal fate and toxicity of Pickering emulsions stabilized by nanoparticles would be beneficial [91]. Another limitation of Pickering emulsions is that they typically contain relatively large oil droplets because the droplets produced during homogenization are usually considerably bigger than the colloidal particles used to coat their surfaces.[92] Thus, rapid creaming or sedimentation may occur in products that have relatively low viscosities. Moreover, the relatively large droplet size may reduce the bioavailability of any encapsulated bioactive substances because the droplets may not be rapidly or fully digested within the human gut. Consequently, there is a need to develop smaller edible colloidal particles and more effective homogenization methods that can be used to successfully prepare Pickering emulsions containing smaller oil droplets. In addition, there is a need to understand how Pickering emulsions behave when incorporated into real food products, especially their interactions with other ingredients and their response to being exposed to food processing operations, prolonged storage, and food preparation procedures.

HIGH INTERNAL PHASE EMULSIONS

HIPE mechanism and formation

High internal phase emulsions (HIPEs) have a droplet concentration that exceeds the close packing limit, which is around 74% v/v.[93] At these high concentrations, the droplets are often deformed into polyhedral shapes that are separated by thin films of continuous phase (Figure 4, right panel). HIPEs are typically semi-solid materials because the droplets are so closely packed together that they cannot easily move past each other when an external force is applied. Moreover, external energy is required to deform the droplets. Like conventional emulsions, HIPEs are thermodynamically unstable systems, *i.e.,* they have a tendency to revert back to the separated oil and water phases over time. Nevertheless, they can be designed to be kinetically stable (“metastable”), *i.e.,* to persist for a long period of time without changing their properties or breaking down. Unlike dilute emulsions,[5] HIPEs are more resistance to gravitational separation because the droplets cannot easily move upwards or downwards.[6] However, they must be formulated to avoid coalescence and oiling off during storage because the droplets are in close proximity to each other for extended periods. As a result, the type of emulsifiers and other stabilizers used to create HIPEs must be carefully selected.

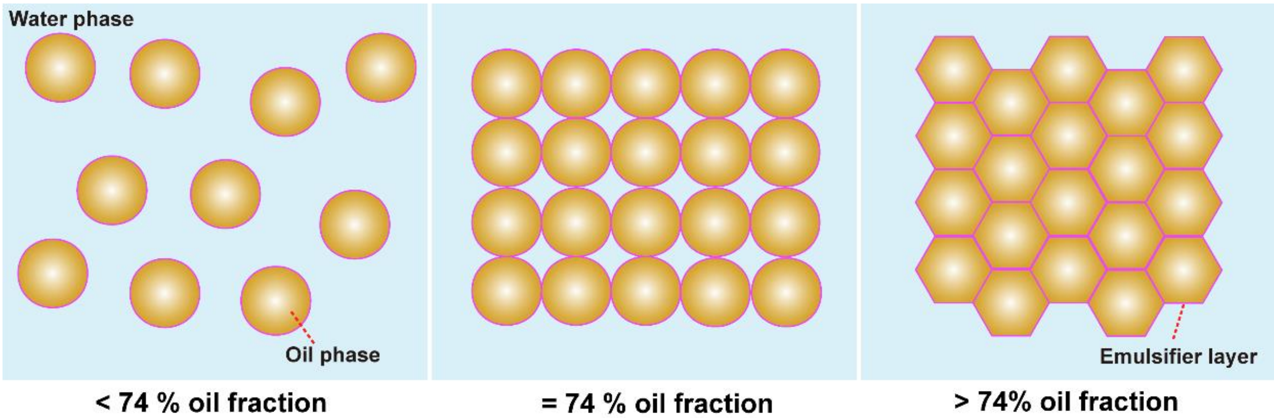

Figure 4. Schematic showing (not to scale) of the oil phase structure of HIPEs at different internal phase volume fractions. Reproduced from ref.94.[93] Copyright 2020 Elsevier.

Typically, HIPEs are fabricated by homogenizing a dispersed phase and a continuous phase containing an appropriate emulsifier. Two different preparation methods are commonly used to achieve this goal: the one-step and two-step methods.[7] The one-step method involves combining the required volumes of continuous and dispersed phases together and then homogenizing, often using a high shear mixer. The two-step method involves gradually adding the dispersed phase to the continuous phase under continuous homogenization (similar to traditional mayonnaise production). The preparation method selected is often determined by the nature of the emulsifier and other stabilizers used. HIPEs can be prepared using some small molecule surfactants,[94] however, the selection of the surfactant type and concentration should be made carefully since phase inversion of the emulsion may occur (*e.g.,* O/W to W/O or *vice versa*) at high droplet concentrations when the surfactant has some solubility in the dispersed phase. Furthermore, the food industry is increasingly looking for alternatives to synthetic surfactants due to consumer concerns about their potential adverse health and environmental effects, especially when used at the high concentrations required to formulate HIPEs.[95] As a result, there are efforts to identify more label friendly emulsifiers that can be used in the food industry to form HIPEs.

Colloidal particles, which may be organic or inorganic, are particularly useful for creating stable HIPEs because they are able to inhibit coalescence of the oil droplets.[93] HIPEs formed using colloidal particles are referred to as high internal phase Pickering emulsions or HIPPEs. Compared to HIPEs formed from molecular emulsifiers, HIPPEs have several potential advantages including higher internal phase volumes, reduced stabilizer levels, higher resistance to coalescence, and greater stability to environmental changes. As a result, the creation and characterization of HIPPEs has been a major focus of recent research in the food, cosmetic, and pharmaceutical industries. In particular, there has been a focus on the development of HIPPEs using natural biopolymers as stabilizers.[96-97] For this reason, the main focus of this section will be on recent research on the development of food-grade HIPPEs from natural stabilizers (Table S1).

Food-grade stabilizers

Polysaccharide-based particles. Similar to dilute Pickering emulsions, colloidal particles that are derived from starch, chitin, and cellulose can also be used to prepare food-grade HIPPEs. Native starch nanocrystals prepared by acid hydrolysis have been reported to be able to form and stabilize soy oil-in-water HIPEs (φ = 75-85%).[98] Increasing the concentration of starch nanocrystals decreased the droplet size and increased the stiffness of the HIPPEs. Chitin nanocrystals have also been used as an efficient stabilizer in HIPPEs (φ = 75%).[7] In our recent study, which utilized a two-step preparation method, a relatively low concentration of chitin nanofibrils (0.064 wt %) was used to form and stabilize HIPPEs (φ = 88%).[8] These HIPPEs were also shown to be physically stable for over 90 days. In a more recent study, octenyl succinic anhydride (OSA)-modified rodlike cellulose nanocrystals were also shown to stabilize HIPPEs (φ = 80%).[99] The droplet size and viscosity of the HIPPEs could be tuned by varying the concentration of colloidal particles used to formulate them, which means their properties could be tailored for different applications.

Protein-based particles. Protein-based stabilizers for HIPPEs can be derived from animal or plant sources. Animal sources include gelatin meat, milk, and egg, whereas plant sources include cereals, legumes, seeds, and nuts. Whey protein microgels or nanoparticles have been successfully used for the preparation and stabilization of HIPPEs.[100] In a recent study, a relatively low concentration of whey protein nanoparticles crosslinked by calcium ions (0.2%) were used to form stable HIPPEs (φ = 80%).[101] These HIPEs remained physically stable for over 60 days, which can be attributed to the reduction in droplet creaming associated with close droplet packing. Ovalbumin was recently used to prepare HIPPEs, which enabled the formation of emulsions with the ability to resist droplet coalescence, lipid oxidation, and oil vaporization.[102] Bovine serum albumin (BSA) glycated with galactose has been shown to form soft colloidal particles that can be used as emulsifiers to prepare HIPPEs that are more stable than those prepared from native BSA.[103] HIPPEs that remained stable during long-term storage, thermal processing, and freeze-thawing could be formed even at relatively low BSA conjugate concentrations (0.1 wt%). Gelatin particles have also been shown to be able to form and stabilize HIPPEs (φ = 80%) at relatively low concentrations.[104-105] In a recent study, a facile and *in situ* method for the preparation of food-grade HIPPEs was developed using sonicated pre-fractured casein flocs.[106] This study demonstrated that an ultrasound treatment is an alternative method to produce protein particle-stabilized HIPPEs.

Various kinds of plant-based proteins have also been used to stabilize HIPPEs. Gliadin, a cereal storage protein, has been used to fabricate colloid particles through antisolvent precipitation, and their ability to form stable HIPPEs (φ = 80%) has been demonstrated.[107] In a recent study, peanut protein microgels (1.5%), which were prepared by transglutaminase cross-linking followed by gel disruption, were also shown to form stable HIPPEs (φ = 87%).[60] The morphology of the droplets in the emulsions could be tuned by changing the pH of the aqueous phase (Figure 5). In a recent study, native soy β-conglycinin was used as a stabilizer to form HIPPEs.[108] Even at a relatively low protein concentration (0.2 wt%), HIPPEs that were stable against heating and prolonged storage (up to 60 days) could be formed. These HIPPEs broke down when exposed to freeze-thawing but they could be re-emulsified again.

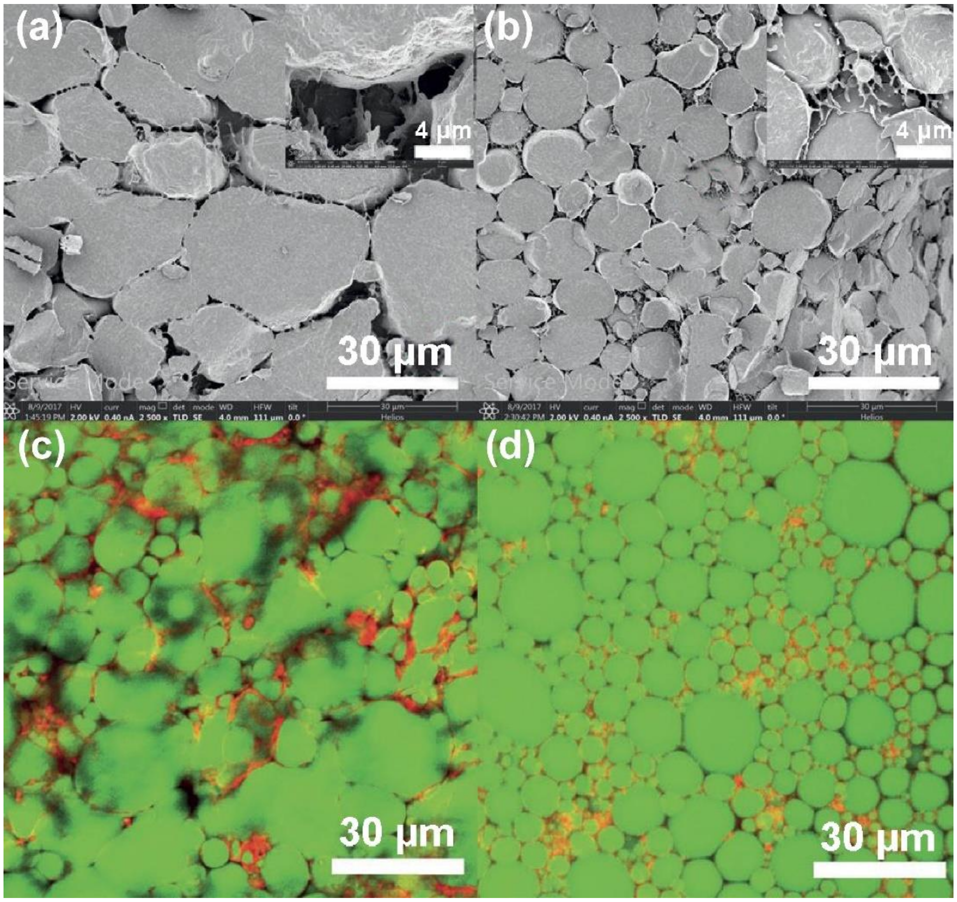

Figure 5. (a) and (b) cryo-SEM and (c) and (d) confocal images of peanut protein isolate microgel-stabilized HIPPEs with 85% cold-pressed peanut oil. Inserts in (a) and (b) are enlarged views. The HIPPEs in (a) and (c) were obtained at pH 3, and in (b) and (d) was obtained at pH 9. In (c) and (d), the oil phase is shown in green and the particles in red. Reproduced from ref.61.[60] Copyright 2018 Wiley.

Composite particles. Colloidal particles comprised of more than one constituent have also been used to form food-grade HIPPEs. Some of the main advantages of using composite colloidal particles for this purpose is their customizable functionality, enhanced stabilizing ability, and diverse range of potential applications. Recently, an all-protein-based composite particle system was developed by combining ovotransferrin and lysozyme through electrostatic attraction.[109] The composite particles obtained were able to stabilize medium chain triacylglycerol oil HIPPEs (φ = 75%) with tunable droplet sizes. The gel-like structure of the HIPPEs formed displayed excellent stability during long-term storage and enhanced bioaccessibility of encapsulated curcumin.[109]

Combinations of proteins and polysaccharides are often used to form composite particles that have better emulsifying properties than the individual components.[103] Recently, a HIPPE (φ = 85%) was prepared using a one-step process that involved simply blending an aqueous solution of gliadin/gum arabic nanoparticles with corn oil.[110] These HIPPEs were relatively stable to pH, ionic strength, and temperature changes. Colloidal particles comprising of soy glycinin glycated to soy polysaccharides have also been used to stabilize HIPPEs (φ = 80%) at relatively low particle concentrations (1 wt%).[111] Soy polysaccharide-soy protein nanoparticles have also been used to form and stabilize HIPPEs, which exhibited good stability over a broad range of temperature, pH, and ionic strength conditions, as well as after drying and freeze-thawing.[112] A zein/pectin composite particle has also been used to form stable HIPPEs.[113] In this study, manipulation of the interfacial self-assembly and packing of composite particles facilitated the formation of a 3D oil droplet network that promoted the formation of HIPEs with strong viscoelasticity, thixotropy and storage stability.

Composite particles consisting of bovine serum albumin and cellulose nanocrystals have also been utilized to create stable HIPPEs. In this system, BSA-covered CNCs were used to create stable, gel-like HIPPEs whose stiffness could be tuned by modulating the ratio of CNCs and BSA used.[114] As well as binary composite particles, ternary composite particles can also be used as stabilizers for HIPPEs. For instance, zein/propylene glycol alginate/rhamnolipid particles have been produced by solvent evaporation.[115] These particles were successfully used to form HIPPEs containing relatively small oil droplets that were stable to coalescence over a wider range of pH values, temperatures, and NaCl concentrations.

Novel applications in foods

Compared to conventional emulsions, HIPEs exhibit high resistance to phase separation, enhanced loading capacity, and tunable semi-solid textural properties, which may be useful in some food applications. Due to their gel-like textures, HIPEs are most suitable for application in food products with this kind of rheological characteristics, such as dressings, mayonnaise, sauces, dips, and spreads.

Encapsulation and delivery. HIPEs are particularly suitable to encapsulate, stabilize, and deliver hydrophobic bioactive ingredients, such as oil-soluble vitamins and nutraceuticals. They typically have a much higher loading capacity than conventional emulsions because of their higher oil contents. In a recent study, thermo-responsive starch particles obtained by nanoprecipitation were used to form stable β-carotene-loaded HIPPEs using soybean oil as a carrier oil.[116] *In vitro* release experiments showed that the release of β-carotene was temperature-dependent, which may be useful for triggered release applications. Using genipin-crosslinked ovotransferrin particles as a stabilizer, a HIPPE-based delivery vehicle for hesperidin has been fabricated.[117] Visual and microscopy analysis indicated that these HIPPEs were stable over a broad range of pH and ionic strength conditions. An *in vitro* digestion study showed that these HIPPEs could improve the bioaccessibility of hesperidin, which can be attributed to the formation of mixed micelles capable of solubilizing this hydrophobic nutraceutical. Whey protein microgel-stabilized HIPPEs have recently been developed to protect probiotics (*Lactobacillus plantarum*) from damage during pasteurization.[118] These HIPPEs enhanced the viability of *Lactobacillus plantarum* (7 CFU/mL) after pasteurization compared to conventional emulsions (3 CFU/mL). The probiotic viability was also shown to increase as the microgel concentration used to fabricate the HIPPEs was increased. This study demonstrated the potential of using HIPPEs to deliver probiotics to the colon, thereby modulating gut health.

HIPEs can also be used to inhibit the chemical degradation of encapsulated bioactive agents during storage and processing. A recent study showed that chitosan/caseinophosphopeptide particles could be used to form HIPPEs, and that these systems were capable of inhibiting the oxidation of linseed oil trapped inside the droplets.[119] The oxidative stability of algae oil has also been shown to be improved when it is encapsulated in HIPPEs stabilized by gliadin/chitosan particles.[120] In addition, curcumin encapsulated within these HIPPEs was shown to have a higher bioaccessibility after *in vitro* digestion then curcumin dispersed in bulk oil.[120] Gelatin particle-stabilized HIPPEs have been shown to protect β-carotene from degradation during storage, which was attributed to the ability of the gelatin particles to scavenge free radicals and inhibit pro-oxidants reaching the carotenoids.[105]

Fat replacement. Many semi-solid foods owe their desirable textural attributes to the presence of a 3D fat crystal network, which often contains saturated or trans fats. Excessive consumption of these fats can lead to an increased risk of cardiovascular disease and diabetes.[6] Therefore, it is important to develop food-grade alternatives to replace saturated and trans fats. It has been reported that the semi-solid textures produced by HIPPEs may be useful as a replacement for those formed by fat crystal networks in some products.[121] For instance, a recent study reported that HIPPEs stabilized by meat protein particles and various types of oils could be used for this purpose (Figure 6).[122]

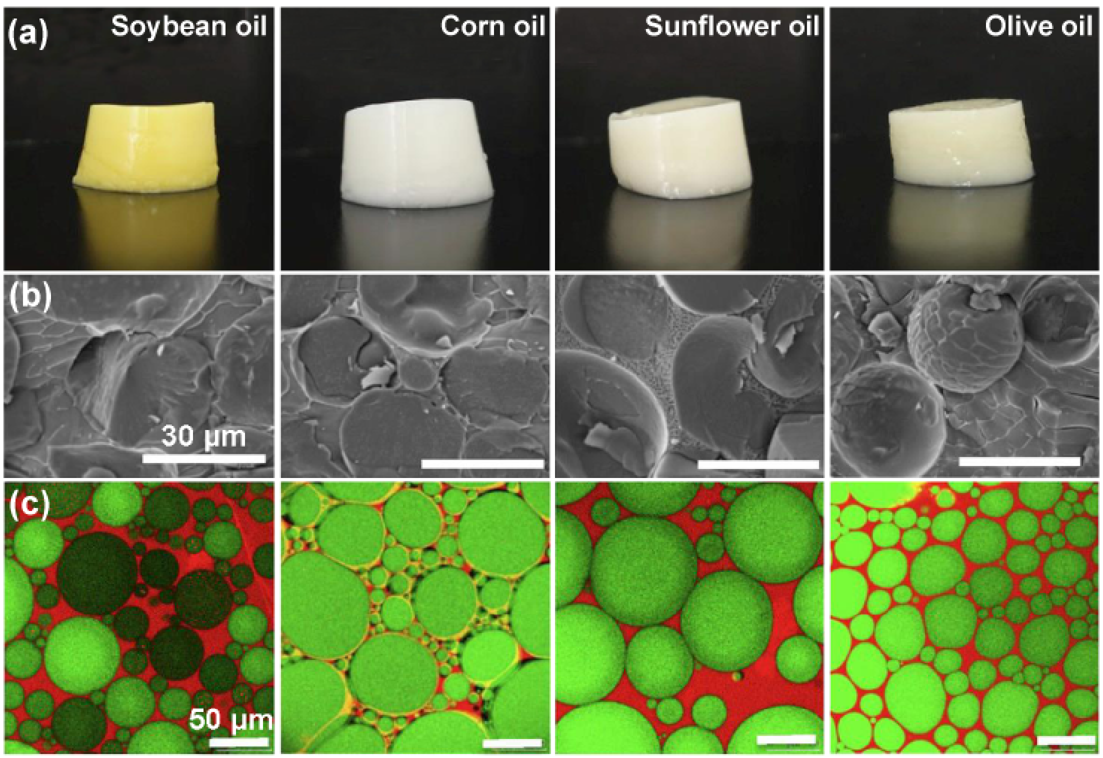

Figure 6. (a) Visual appearance, (b) microstructure and (c) confocal images of HIPPEs formed with soybean oil, corn oil, sunflower oil, and olive oil (from left to right). The protein and oil were dyed with Nile red and Nile blue, respectively. Reproduced from ref.123.[122] Copyright 2020 Elsevier.

Zein-sodium caseinate-propylene glycol alginate particles have been used to form semi-solid HIPPEs (φ = 80%) with textures and appearances similar to mayonnaise.[123] HIPPEs stabilized by wheat gluten particles have been developed as a plant-based mayonnaise substitute.[124] The HIPPEs showed similar textural properties to mayonnaise, such as sliminess, creaminess, and smoothness, but a much better thermal stability. In another study, semi-solid plant-based HIPPEs (φ = 75%) stabilized by citrus fiber/corn peptide particles were prepared,[125] which exhibited good heat and freeze-thaw stability. In comparison to an egg-based commercial mayonnaise, the plant-based HIPPEs exhibited much less friction, suggesting that they might provide more creaminess and smoothness. This technology may therefore be useful for creating high quality plant-based foods.

3D-printed foods. 3D printing technology has increasingly attracted significant attention for its use in additive manufacturing because it provides customizability and flexibility for fabricating structures with arbitrary shapes.[126] In the food industry, 3D-printing has been recognized as a promising tool for creating a new generation of customizable food products.[127] In 3D printing, the rheological behavior of the "food inks" is critical to the successful creation of a high quality product.[128] The semi-solid behavior exhibited by HIPPEs makes them good candidates for the creation of versatile food inks. Recently, the influence of particle properties on the rheological behavior of HIPPEs stabilized by zein/tannic acid particles was reported.[129] The storage modulus of the HIPPEs could be adjusted by modulating the colloidal particle properties. A recent study showed that HIPPEs stabilized by zein-propylene glycol alginate-rhamnolipid particles could be made to change from fluid to solid by adding NaCl, which offered a novel strategy for adjusting their rheological behavior.[115]

HIPPEs (φ = 85%) stabilized by cod protein particles (10-50 mg/mL) have also been investigated for their potential use as food inks. The yield stress and shear thinning behavior of the HIPPEs could be modulated by adjusting the concentration of cod protein particles used, thereby leading to food inks with printability and extrudability characteristics suitable for 3D printing.[130] In our recent study, a 3D printable ink that consisted of chitin nanofibril-stabilized HIPPEs (φ = 88%) was developed.[8] The rheological properties of these food inks could be tuned by varying pH values because this altered surface energy of chitin nanofibrils due to protonation/deprotonation of the amino groups. These HIPPEs could be used to create edible products with specific shapes by taking advantage of their viscoelastic behavior (Figure 7a). These polysaccharide-based HIPPEs have also been shown to be suitable as food inks for 3D printing *via* direct ink writing (Figure 7b and 7c), which opens up new avenues for creating novel functional foods.

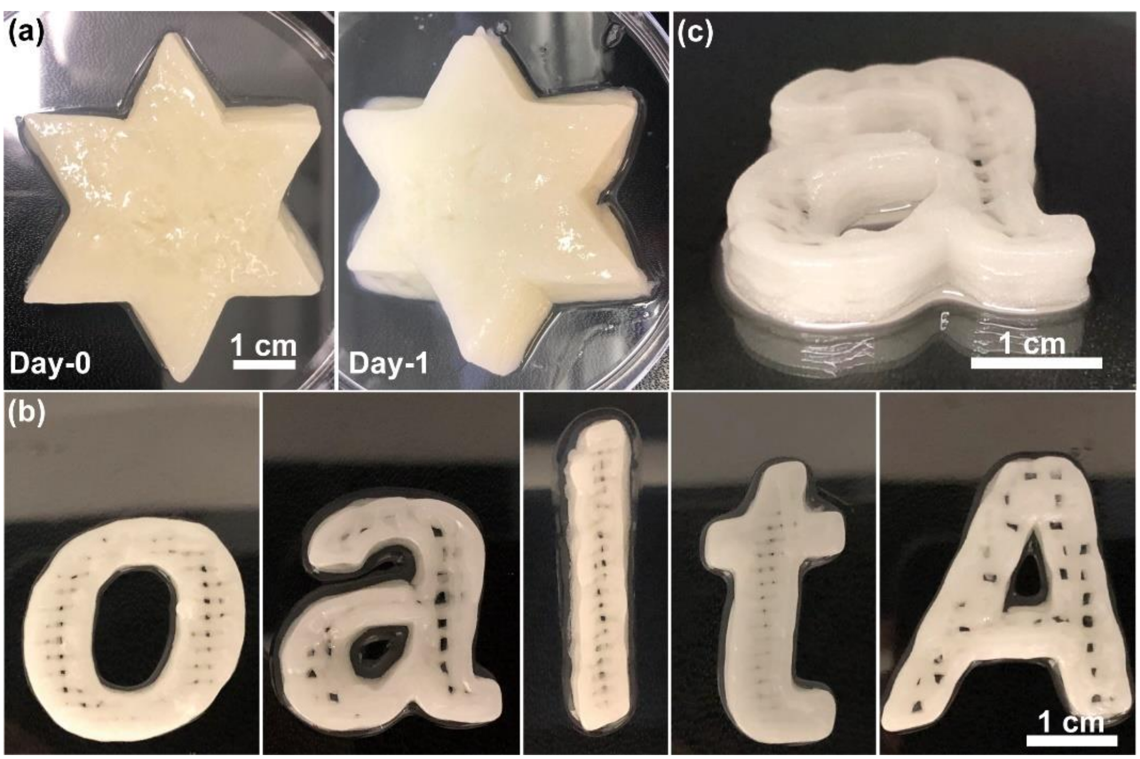

Figure 7. (a)-(c) 3D printed objects from food-grade HIPPEs that were stabilized by chitin nanofibrils at 88% sunflower oil volume fraction. Reproduced from ref.8.[8] Copyright 2020 American Chemical Society.

Current and future perspectives

In this section, the advantages and disadvantages of using HIPEs in foods are discussed, as well as areas where research is needed in the future. The novel functional attributes of HIPEs are mainly related to their extremely high dispersed volume fraction, which leads to semi-solid textural characteristics, strong resistance to gravitational separation, and a high loading capacity. As a consequence, HIPEs are particularly suitable for food applications where semi-solid textures are required, such as dressings, mayonnaise, dressings, or desserts. Moreover, they are useful for applications where high levels of non-polar bioactive substances need to be encapsulated.[131] As mentioned earlier, the fact that HIPEs can flow when low stresses are applied to them but they set when these stresses are removed, means they are particularly suitable for utilization as edible inks for the 3D printing of foods.[132]

One of the main limitations of using O/W HIPEs in food applications is that they have a very high fat content, which may be problematic from a nutritional viewpoint. Conversely, W/O HIPES may be used to create low-fat and low-calorie versions of highly viscous or semi-solid fatty products like spreads, mayonnaise, and dressings. Another challenge is that HIPEs prepared using molecular emulsifiers are highly unstable to coalescence during long-term storage because their droplets are forced together over long periods. For this reason, Pickering emulsifiers are often required to form HIPEs that are more resistant to coalescence. As will other types of advanced emulsion technologies, it will be important in the future to establish how they behave in real foods and when exposed to food processing, storage, and preparation conditions. Moreover, more research is required to understand how they behave within the gastrointestinal tract, such as their impact on lipid digestion and bioactive bioavailability.

NANOEMULSIONS

Nanoemulsion mechanism and formation

Nanoemulsions are like conventional emulsions but they contain smaller droplets, typically having mean diameters below about 200 nm.[9] The relatively small size of the droplets in these systems provides some potentially beneficial physicochemical and functional attributes,[134] including greater resistance to gravitational separation and aggregation, increased surface reactivity, enhanced encapsulating properties, improved bioavailability, and good optical clarity.[135] Even so, nanoemulsions are still thermodynamically unfavorable systems because of their positive surface free energy and high surface area. Consequently, they still have a tendency to break down over time as a result of gravitational separation, flocculation, coalescence, and/or Ostwald ripening (Figure 8).[136] Nevertheless, the rates of these processes are usually considerably different in nanoemulsions than in conventional emulsions because of particle size and curvature effects.[137] For example, nanoemulsions are often more stable to gravitational separation, flocculation and coalescence, but less stable to Ostwald ripening. For this reason, a major focus in this area is the creation of nanoemulsions that have a sufficiently long kinetic stability for commercial applications.

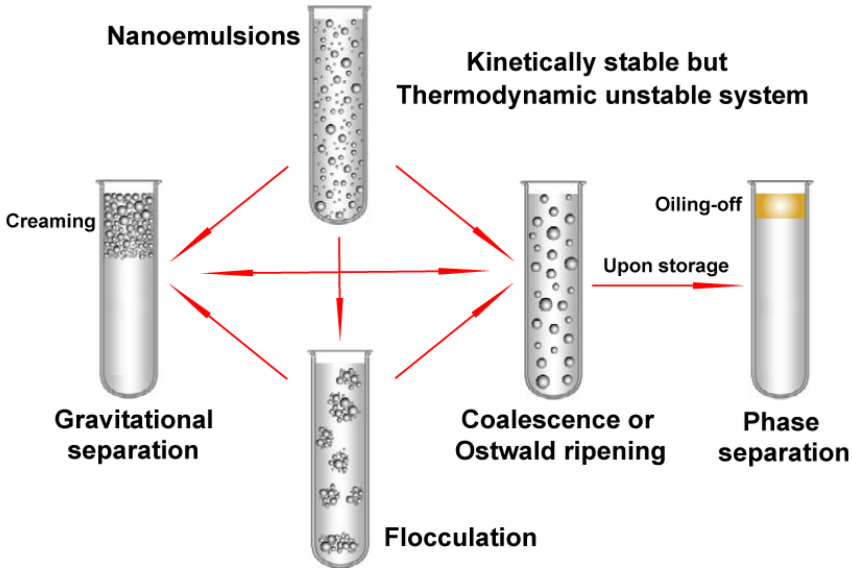

Figure 8. Nanoemulsions may break down through a variety of different physicochemical mechanisms, depending on the composition and structure, as well as exposing to specific environmental conditions. Reproduced from ref.137.[136] Copyright 2018 Elsevier.

Nanoemulsions can be prepared using various approaches, which are conveniently categorized as high- or low-energy approaches.[9, 138] High-energy approaches are the most widely used for producing nanoemulsions in industrial applications. They involve the utilization of mechanical machines that are designed to create intense disruptive forces (such as shear, turbulent, and cavitation forces) that break up the oil and water phases,[139] leading to the formation of tiny oil droplets. The most common mechanical machines used for producing nanoemulsions are high-pressure valve homogenization,[140] microfluidization,[141] rotor-stator homogenization,[142] and sonication.[143] There are typically relatively high equipment and operating costs associated with high-energy emulsification methods, which are a disadvantage for some applications. However, there are also numerous advantages that counterbalance these drawbacks for most food applications. They are capable of homogenizing a broad range of oils, using a wide range of different emulsifiers. Moreover, they are capable of continuous production of nanoemulsions at relatively high throughputs. Low-energy approaches often rely on the spontaneous generation of tiny droplets in certain surfactant-oil-water mixtures when their composition or environment is altered in a controlled manner.[144] The driving force for nanoemulsion formation in this case is the release of the internal chemical energy during emulsification.[145] The most commonly used low-energy approaches are spontaneous emulsification,[146] emulsion inversion point,[147] and phase inversion temperature/composition methods.[148-149] Compared to the high-energy approaches, the advantages of low-energy ones are that they are simple to implement and no expensive equipment is required. However, high levels of surfactant, especially synthetic ones, are typically required to produce nanoemulsions by low-energy approaches, which limits their application in many products due to cost, taste, and toxicity reasons.

Nanoemulsion ingredients

Emulsifiers and other stabilizers are often required to prepare nanoemulsions with desirable functional attributes and extended shelf lives. Due to changing consumer preferences, there has been a strong emphasis on the creation of nanoemulsions from natural label-friendly ingredients, rather than synthetic ones. In this section, we therefore provide an overview of the key ingredients required to form and stabilize nanoemulsion, with an emphasis on natural ones.

Emulsifiers. Emulsifiers are amphiphilic molecules that adsorb to the surfaces of the droplets formed during homogenization, reduce the interfacial tension, and form a protective coating that inhibits their aggregation.[69] Typically, emulsifier-coated oil droplets are protected from aggregation by generating steric and/or electrostatic repulsive forces, whose magnitudes depend on interfacial characteristics like thickness, packing, polarity, and charge. The selection of a suitable emulsifier for a specific nanoemulsion application depends on its molecular and physicochemical attributes,[150] as well as its ease of utilization, legal status, and cost.[151] A number of different kinds of natural emulsifier have been identified and successfully applied to form and stabilize food-grade nanoemulsions, including polysaccharides, proteins, phospholipids, and biosurfactants (Table S1).[152] The abilities of emulsifiers to form and stabilize nanoemulsions varies, and so it is critical to identify the most appropriate one for specific applications. In our recent study, the relatively effectiveness of different natural emulsifiers (soy lecithin, gum arabic, quillaja saponin, and whey protein) at fabricating corn oil-in-water nanoemulsions using microfluidization was compared.[153] Although there were distinct differences in emulsifier surface activity (Figure 9a), they could all form stable nanoemulsions, but different amounts were needed to create small droplets (Figure 9b). This study highlighted the capability of natural emulsifiers for efficiently producing label-friendly nanoemulsions.

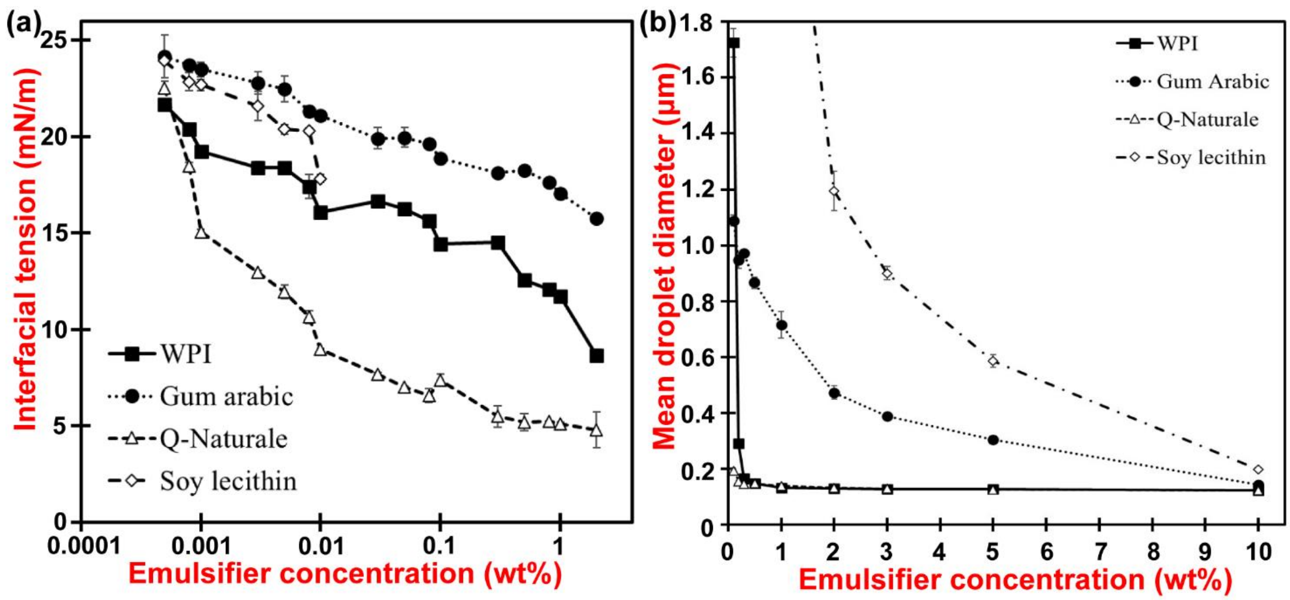

Figure 9. Influence of emulsifier type (whey protein isolate WPI, gum arabic, quillaja saponin, and soy lecithin) and concentration on (a) the interfacial tension at corn oil-water interface and (b) the mean particle diameter of corn oil-in-water nanoemulsions produced by microfluidization. Reproduced from ref.154.[153] Copyright 2016 Elsevier.

Texture modifier. A texture modifier is sometimes incorporated into the aqueous phase of a nanoemulsion to alter its rheological properties, with the aim of prolonging its shelf life or providing desirable textural attributes.[69] Two types of texture modifier are typically used for this purpose: thickening agents and gelling agents. A thickening agent increases the shear viscosity of a solution because it alters the fluid flow profile, thereby leading to more energy dissipation. Typically, thickening agents are soluble biopolymers with extended molecular structures.[154] Commercially, water-soluble polysaccharides, such as xanthan, guar, and gellan gums, are frequently used as thickening agents because they can greatly thicken solutions when added at low concentrations.[155] Gelling agents are used to create semi-solid properties in aqueous solutions be forming a 3D network of cross-linked or overlapping biopolymers or colloidal particles. In food industry, proteins and polysaccharides are typically used as gelling agents in nanoemulsions. Texture modifiers can increase the shelf life of nanoemulsions by slowing down droplet movement, thereby inhibiting gravitational separation and droplet aggregation. As an example, polysaccharide-based texture modifiers have been shown to improve the stability of essential oil-in-water nanoemulsions by increasing the viscosity of the aqueous phase.[156]

Weighting agents. A weighting agent is a substance that is added to the dispersed phase of a nanoemulsion so as to match its density to that of the continuous phase, thereby reducing the driving force for gravitational separation.[69] In most nanoemulsions, the density of the oil phase is less than that of the aqueous phase. Consequently, weighting agents tend to be dense hydrophobic substances that are edible like sucrose acetate isobutyrate, brominated vegetable oil, and ester gum.[157]

Ripening inhibitor. A ripening inhibitor is an additive that is incorporated into the dispersed phase of \nanoemulsions to restrict droplet growth through Ostwald ripening.[158] The application of these additives is most important in O/W nanoemulsions formulated from oils that have some solubility within water, including essential oils and flavor oils.[159] Without a ripening inhibitor, these kinds of nanoemulsions would quickly breakdown as a result of the oil molecules moving from the smaller oil droplets to the larger ones, as this phenomenon leads to a net increase in droplet dimensions. A ripening inhibitor is typically an oil-soluble substance that has an extremely low water-solubility, *e.g.,* long-chain triacylglycerol oils like corn oil, sunflower oil, or mineral oil.[160] The incorporation of a ripening inhibitor into the oil phase slows down Ostwald ripening due to an entropy of mixing phenomenon. When the oil molecules move from the smaller to larger droplets, there is a rise in the concentration of the ripening inhibitor inside the smaller droplets. This results in a concentration gradient that favors the transport of oil molecules from the large droplets to the smaller ones, thereby opposing droplet growth.[161] A recent study showed that the stability of antimicrobial nanoemulsions formulated from essential oils could be improved by incorporating appropriate types and amounts of ripening inhibitors.[162]

Novel applications in foods

The small droplet dimensions and high surface area of nanoemulsions makes them especially suited for specific applications within the food industry.[9, 163] A few examples of the potential application of nanoemulsions in foods are highlighted in this section.

Encapsulation and delivery systems. Oil-in-water nanoemulsions are especially suited for introducing hydrophobic substances (such as vitamins, nutraceuticals, antioxidants, antimicrobials, colors, or flavors) into aqueous-based food and beverage products.[164] The hydrophobic substances are mixed with the oil phase prior to homogenization, which leads to the formation of nanoemulsions containing active-loaded oil droplets dispersed in water. Nanoemulsions that are optically clear or only slightly turbid can be produced by ensuring that the mean droplet diameter is much smaller than the wavelength of light ($d <$ 50 nm), which is valuable for incorporating hydrophobic substances into transparent food or beverage products.[9, 163] The strong resistance of nanoemulsions to gravitational separation and droplet aggregation is beneficial for products that require a long shelf. Moreover, nanoemulsions can be designed to be more resistant to environmental stresses than conventional emulsions. For instance, a recent study used whey protein isolate (WPI) as a natural emulsifier to form nanoemulsions loaded with vitamin E-acetate.[165] These nanoemulsion were shown to be stable against flocculation when exposed to a wide range of environmental conditions.

Due to their small droplet size and high surface area, nanoemulsions tend to be rapidly digested by lipases in the gastrointestinal tract.[163] This phenomenon leads to rapid release and solubilization of encapsulated hydrophobic substances, which significantly increases their bioaccessibility and bioavailability. As an example, the impact of digestion on the bioavailability of coenzyme Q10 loaded into nanoemulsions was evaluated using a simulated gastrointestinal tract.[166] The bioavailability of coenzyme Q10 was 1.8-fold higher when it was delivered in nanoemulsion-form than in bulk oil-form.

Nanoemulsions can also be used to improve the efficacy of antimicrobial essential oils against a broad range of microorganisms, including bacteria, yeast, and molds. This is because nanoemulsions increase the water-dispersibility and transport properties of the essential oils, thereby increasing their ability to disrupt the cell membranes of the microorganisms.[167] As an example, thyme oil-loaded nanoemulsions were recently developed that exhibited good antibacterial activity against two model food pathogens: *E. coli* and *S. aureus*.[168] These results highlight the utility of using nanoemulsions to create antimicrobial delivery systems for use in foods.

Fat and calorie reduction. Nanoemulsions can be used as building blocks for creating novel structures and textures in foods.[169] In particular, nanoemulsions exhibit solid-like characteristics at much lower concentrations than conventional emulsions with the same compositions.[170] This phenomenon may be useful for creating reduced calorie products that are viscous or gel-like, *e.g.,* sauces, dips, spreads, and dressings. The ability of nanoemulsions to gain solid-like characteristics at low droplet concentrations may arise due to various physicochemical phenomenon (Figure 10): (a) *repulsive gelation*: when there are long-range repulsive interactions between droplets, these become more important when the droplet size shrinks, causing the droplets to become jammed together;[171] (b) *attractive gelation*: when there are attractive interactions between similar kinds of droplets, they tend to aggregate, with smaller droplets forming 3D networks at lower droplet concentrations;[154] and, (c) *heteroaggregation gelation*: when two populations of oppositely charged nanoemulsion droplets are mixed together they tend to aggregate and form a 3D particle network.[172] Nanoemulsion gels with different textural attributes can be created by controlling droplet size, concentration, and charge.[173]

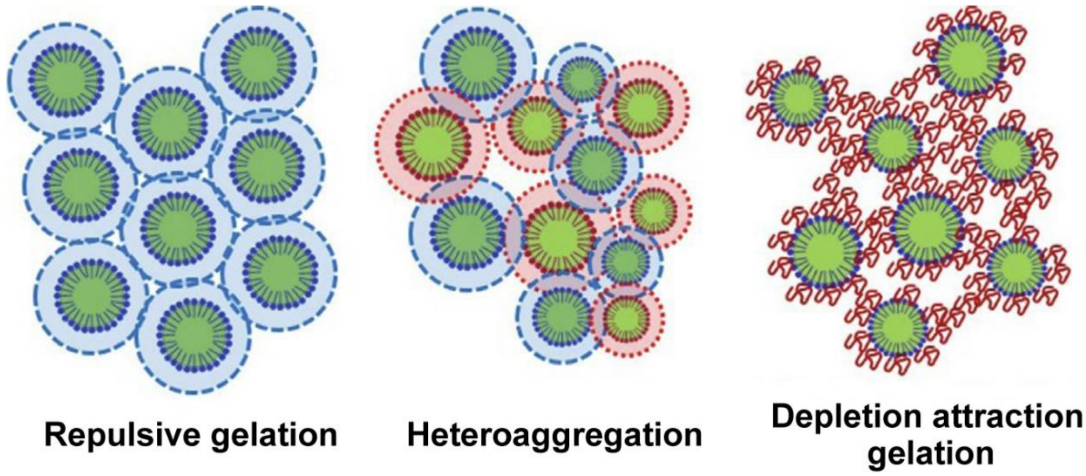

Figure 10. Schematic showing (not to scale) of the possible gelation processes of nanoemulsion droplets. Reproduced from ref.175.[174] Copyright 2018 Elsevier.

Current and future perspectives

In this section, the benefits and limitations of nanoemulsions for food applications are discussed, as well as the needs for future research. The main advantages of using nanoemulsions are related to the extremely small dimensions of the fat droplets, which leads to greater resistance to creaming and aggregation, enhanced optical clarity, and increased bioavailability of encapsulated hydrophobic bioactives. It should be noted that nanoemulsions can be formulated entirely from plant-derived ingredients, which is important for the growing market in plant-based foods.[175-176] Some of the main limitations of using nanoemulsions in the food industry are associated with the fabrication methods required. For low-energy emulsification methods, high concentrations of synthetic surfactants are required, which is not desirable from a health, cost, or flavor perspective. In contrast, for high-energy emulsification methods, specialized mechanical methods are required, which are often expensive to purchase and maintain. Another potential challenge is the regulations associated with incorporating nanoparticles into foods in some countries. In the future, more research is required to understand how nanoemulsions behave in real foods and to understand the gastrointestinal fate using *in vitro* and *in vivo* studies.

MULTIPLE EMULSIONS

Multiple emulsion mechanism and formation

Multiple emulsions consist of small droplets of one immiscible substance embedded within larger droplets of another immiscible substance, which are themselves dispersed within another immiscible substance (that may be similar or different to the first one).[179] The unique structure of multiple emulsions makes them particularly suitable for certain food applications, including the development of reduced-fat food emulsions, flavor masking, triggered release, and the delivery of oil- and/or water-soluble active substances.[180-182]

Different kinds of multiple emulsions can be formulated but water-in-oil-in-water ($W_1/O/W_2$) emulsions are currently the most commonly employed in foods, where W_1 represents the inner water phase, W_2 the outer water phase, and O the oil phase. Multiple emulsions have two different interfacial boundaries that need stabilizing: the W_1-O layer for the inner water droplets and the O-W_2 layer for the oil droplets. As a result, two different types of emulsifier are typically needed to form and stabilize multiple emulsions (Table S1). A more hydrophobic emulsifier is used to coat the surfaces of the inner water droplets (W_1-O), whereas a more hydrophilic emulsifier is used to coat the surfaces of the oil droplets (O-W_2).[179] Like conventional emulsions, multiple emulsions are thermodynamically unstable and are therefore prone to failure during processing, storage, and utilization.[179] In addition to the usual emulsion breakdown mechanisms, such as creaming, flocculation, coalescence and Ostwald ripening, multiple emulsions may also breakdown because the internal water droplets are released, collapse, expand, or aggregate. Numerous strategies have been identified to tackle these issues,[179] including optimization of hydrophobic and hydrophilic emulsifiers, adding weighting agents and ripening inhibitors, gelling the internal water phase, crystallizing the oil phase, and osmotic balancing of the internal and external water phases to prevent water diffusion. In this section, the production and potential applications of multiple emulsions in foods are discussed.

Multiple emulsion production

Multiple emulsions are commonly produced using a two-step homogenization procedure (Figure 11). First, a W_1/O emulsion is prepared by blending water, oil, and a hydrophobic emulsifier together. Second, a W_1/O/W_2 emulsion is produced by blending the W_1/O emulsion, water, and a hydrophilic emulsifier together.[183] The emulsification conditions in the second step should be less intense than those used in the first step, otherwise the W_1/O droplets may be broken down and released. For example, a flavonoid-loaded multiple emulsion was recently prepared using a high-intensity jet homogenizer for the first-step and a low-intensity spinning disc reactor for the second step.[184] The dimensions of the water droplets in the W_1/O emulsion and of the oil droplets in the W_1/O/W_2 emulsion can be controlled by varying the type and concentration of emulsifiers, as well as the homogenization conditions used in the two steps. Moreover, oil and water phase compositions can be varied. Thus, multiple emulsions with different compositions and microstructures can be created, which allows one to tailor them for different functional applications. For instance, the two-step method has been used to prepare W/O/W emulsions with a gelled internal water phase using whey protein as a gelling agent, and polyglycerol polyricinoleate, and Tween 80 as hydrophobic and hydrophilic emulsifiers, respectively.[185] The gelation of whey protein within the internal droplets significantly altered the microstructure of the multiple emulsions, which made it possible to produce model foods with novel textural attributes.[186]

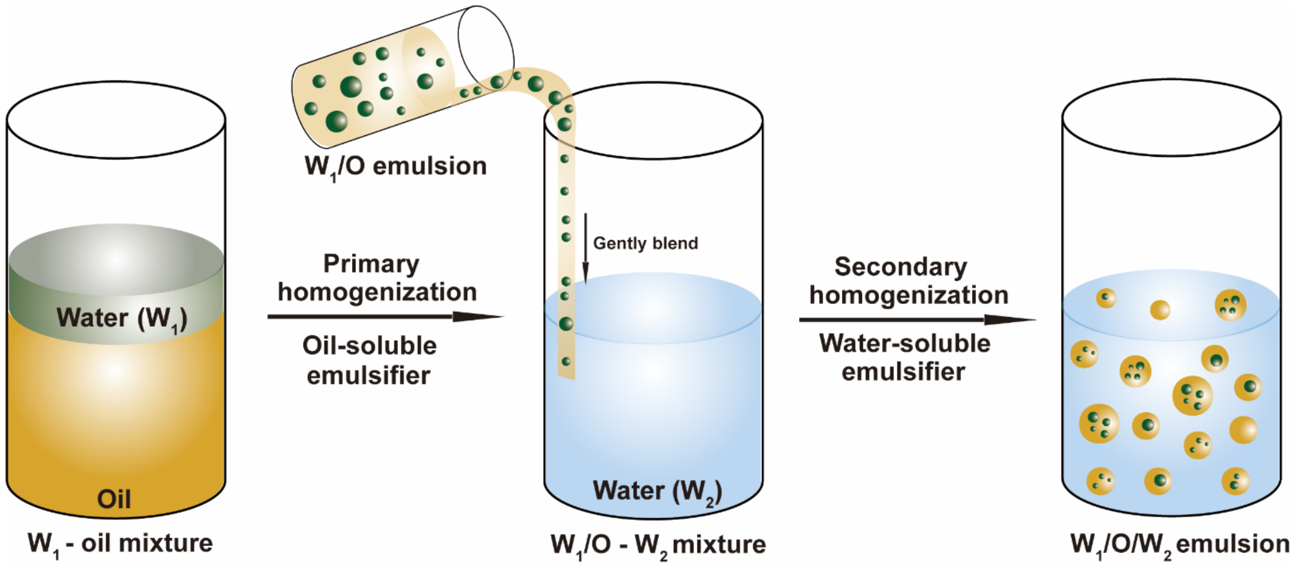

Figure 11. Schematic diagram showing production of multiple emulsions (W_1/O/W_2) using the two-step emulsification procedure. This process requires serial addition of immiscible phases. Homogenization in each step may be carried out using a variety of devices.

Microfluidic devices have been successfully used to produce multiple emulsions with uniform droplet sizes,[187] which may have potential for some food applications.[188-189] Based on the geometries of these devices, two microfluidic emulsification methods have been developed to fabricate multiple emulsions: two-step and one-step processes.[190] The two - step process generates W_1/O droplets first and then disperses them in the continuous phase (W_2) using two sequential microfluidic modules. The one - step process directly produces multiple emulsions by synchronized emulsification of inner (W_1) and middle (O) fluids under the shear of the continuous phase (W_2). Microfluidic emulsification devices allow precise control over the composition, dimensions, and internal structure of multiple emulsions. For example, monodispersed W_1/O/W_2 emulsions consisting of oil droplets that contained one or more internal water droplets were recently created using a starch-based particle emulsifier.[191]

Novel application in foods

Multiple emulsions have a number of potential applications in foods where they have advantages over conventional emulsions.

Encapsulation and delivery. Multiple emulsions can be used to encapsulate, protect, and deliver sensitive functional components such as antioxidants, antimicrobials, flavors, colors, vitamins, minerals, and nutraceuticals. Sensitive hydrophilic components can be loaded into the inner water droplets at high encapsulation efficiencies, where they may be protected from their environment.[192] As an example, multiple emulsions stabilized by nonionic surfactants and protein/polysaccharide complexes were recently used to encapsulate and protect saffron.[193] These multiple emulsions were shown to protect saffron during storage, but then release it under gastrointestinal conditions. The release of encapsulated components within the internal water phase can also be designed to be triggered by specific environmental stimuli, such as in pH, ionic strength, temperature, surface active components, or enzyme activities, thereby achieving responsive delivery platform.[194]

Multiple emulsions can also be used as dual-delivery systems that encapsulate both water-soluble and oil-soluble bioactives.[181, 195] In a recent study, particle-stabilized $W_1/O/W_2$ emulsion gels designed for this purpose were fabricated using a two-step procedure.[196] First, a W_1/O emulsion was formed that contained saccharose and gelatin in the internal aqueous phase and polyglycerol polyricinoleate (a hydrophobic emulsifier) in the oil phase (Figure 12a). Second, the W_1/O emulsion was homogenized with an external water phase containing wheat gliadin nanoparticles (a hydrophilic emulsifier). After preparation, the gelation of the gliadin nanoparticles in the external aqueous phase led to the formation of particle-stabilized $W_1/O/W_2$ emulsion gels with good stability to phase separation (Figure 12b). The authors showed that these emulsions could be used to trap a hydrophilic bioactive (epigallocatechin-3-gallate, EGCG) in the internal aqueous phase and a hydrophobic bioactive (quercetin) in the oil phase (Figure 12c). The chemical stability of EGCG and the solubility of quercetin were improved under simulated gastrointestinal conditions, thereby increasing their bioaccessibilities.[196] This study therefore highlights the potential of multiple emulsions as food-grade delivery vehicles for co-loading multiple bioactives.

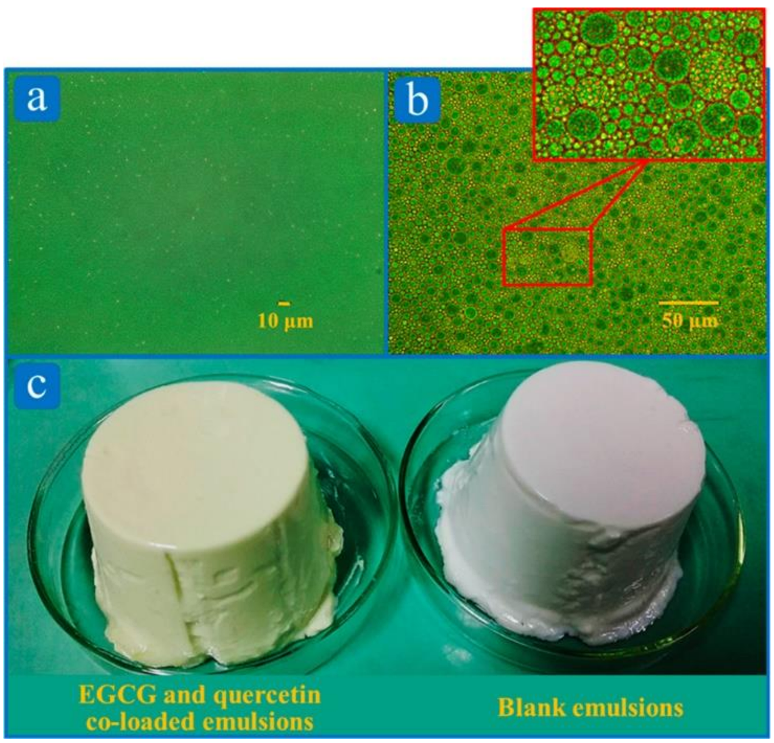

Figure 12. Optical microscopic image of (a) W_1/O emulsion droplets and (b) $W_1/O/W_2$ emulsion gels. (c) Visual appearance of W/O/W emulsion gels. Reproduced from ref.197.[196] Copyright 2018 American Chemical Society.

Recently, a $W_1/O/W_2$ emulsion was fabricated using 2 wt% polyglycerol polyricinoleate as a hydrophobic surfactant and 2 wt% saponin as a hydrophilic surfactant, with iron (ferrous sulfate) encapsulated in the inner aqueous phase.[197] The anionic saponin-coated oil droplets in these multiple emulsions were further coated with a layer of cationic chitosan to increase the resistance of the droplets to aggregation. The $W_1/O/W_2$ emulsions were highly effective at retaining iron within the internal water phase. Indeed, the iron even remained stable when the emulsions were exposed to an osmotic stress gradient, which was attributed to the protective chitosan coatings.

Anthocyanins have been identified as plant-derived pigments that exhibit strong antioxidant, anticarcinogenic, and immune modulating effects, but they are extremely unstable when extracted from their natural environment.[198] Encapsulating them in multiple emulsions has been explored as a way to stabilize them for use in functional foods.[198] A recent study showed the possibility of protecting anthocyanin from degradation by encapsulating them within the inner water phase of a multiple emulsion using polyglycerol polyricinoleate as a hydrophobic emulsifier and quillaja saponin as a hydrophilic emulsifier.[199] These results indicated that anthocyanin encapsulation in the multiple emulsions significantly slowed down pH-induced color changes, which suggested that multiple emulsions may be useful for protection of natural colors.

Another advantage of multiple emulsions is that hydrophilic cargos can be protected from chemical degradation by incorporating them in the inner aqueous phase, which isolates them from other water-soluble ingredients in the outer water phase that they might otherwise react with.[200] This unique function has been demonstrated by a multiple emulsion delivery system encapsulating fish oil in the inner water phase, where the oxidation stability of the fish oil was significantly improved.[201] Another application is to encapsulate hydrophilic ingredients that have undesirable sensory qualities (*e.g.,* bitter, astringent, or metallic flavors) in the inner water phase so that they are not perceived in the mouth during mastication.

Fat and salt replacement. Multiple emulsions can be used to produce healthier foods, *e.g.,* the formulation of foods with reduced fat or sodium levels. The overall fat and calorie content of emulsified foods can be reduced by incorporating water droplets into the oil phase. Moreover, the viscosity of multiple emulsions is usually higher than the that of the conventional emulsions with the same fat contents,[202] leading to a fact that the physicochemical and sensory properties of multiple emulsions are similar as full-fat products, showing the implications for the development of products with reduced fat.[203] Reduced-fat cheeses have been formulated using $W_1/O/W_2$ emulsions stabilized with hydrocolloids, which mimicked some of the desirable textural characteristics of their full-fat counterparts.[204] In a similar study, a multiple emulsion prepared from soybean milk and sunflower oil was used as a reduced-fat substitute for whipped dairy cream.[205] Another study reported the use of multiple emulsions to formulate reduced-fat meat batters, which exhibited stability, cooking yield, hardness and lightness values similar to the control.[206] Other researchers have shown that the bioactives from berries can be encapsulated in the internal aqueous phase of multiple emulsions, which led to a prolonged antioxidative effect.

Over-consumption of salt (sodium) is a major factor contributing to increases in blood pressure and cardiovascular disease.[207] Consequently, it is important for food manufacturers to develop products with reduced sodium levels, without changing their sensory acceptability to consumers. Multiple emulsions have the potential to reduce sodium levels in foods since salt can be encapsulated within the internal aqueous phase and released in burst in the mouth.[203] A recent study addressed the correlation between the physical characteristics of multiple emulsions and the sensory perception of salt.[208] The multiple emulsions were prepared using different volumes of the internal aqueous phase but the same fat and sodium contents. It was found that the saltiness perception could be modulated by changing the structure of the multiple emulsions, which may be useful for developing reduced sodium foods.

Current and future perspectives

The potential advantages and disadvantages of using multiple emulsions in food applications are discussed in this section, as well as possible areas for future research. One of the most promising applications of multiple emulsions is for the creation of reduced calorie products, since some of the oil within the disperse phase of O/W emulsions can be replaced with water, without altering the overall disperse phase volume fraction. As a result, reduced-fat products with similar textures and optical properties as the original version can be produced. Another unique aspect of multiple emulsions is that they contain multiple phases within a single system, which is useful for the encapsulation, protection and release of multiple active ingredients.[209-210] For instance, hydrophilic substances can be trapped within the internal water phase of W/O/W emulsions, while hydrophobic ones can be trapped within the oil phase of the same system.[211] The internal aqueous phase can also be used for flavor masking purposes, *e.g.,* by trapping bitter peptides within it so they are not exposed to the tongue during mastication. Moreover, active ingredients encapsulated within the internal aqueous phase can be released in response to specific environmental triggers, such as changes in temperature, osmotic stress, or enzyme activiy, which may be beneficial for some applications. The main disadvantage of multiple emulsions is that two homogenization steps and two types of emulsifier are used to fabricate them, leading to more production time and costs. Moreover, the final product is often less robust than other forms of emulsions because there are a number of additional instability mechanisms. In addition, there are only a limited number of hydrophobic emulsifiers suitable for application in W/O/W emulsions, with the most effective being synthetic surfactants (such as PGPR), which are not label friendly. Consequently, further research is needed to find more label friendly, preferably plant-based, emulsifiers for utilization within multiple emulsions. As will the other kinds of advanced emulsion technologies it is important to carry out more research on their performance in real food products, as well as to understand the impact of their composition and structure on their sensory perception and gastrointestinal fate.

CONCLUSIONS AND FUTURE OPPORTUNITIES

There have been a number of important advances in emulsion science and technology that can be applied within the food industry to improve the quality, sustainability, or healthiness of foods. For instance, Pickering emulsions and HIPEs that are semi-solid materials with a high resistance to coalescence during storage and processing can be produced from food-grade colloidal particles. These types of emulsion are useful in applications where highly viscous or gel-like foods are required, such as dressings, mayonnaise, sauces, desserts, and dips. Nanoemulsions are particularly useful in low-viscosity products where good resistance to creaming and aggregation is required during storage, which can be achieved because of their small droplet sizes. Moreover, these systems are useful when one needs to incorporate an oil-soluble substance into a transparent aqueous-based product, such as a vitamin-fortified water. In addition, nanoemulsions are particularly useful if rapid release or a high bioavailability of an encapsulated substance is required because they are rapidly digested under gastrointestinal conditions. Multiple emulsions may also have some niche applications in the food industry, such as creating reduced calorie products, co-encapsulation of multiple ingredients, and flavor masking purposes. One of the main challenges now is to translate much of the work that has been carried out in research and development laboratories into large scale commercial production of these novel emulsions. As colloid and interface science advances there are likely to be other new emulsion technologies developed that may also be advantageous for utilization in the food industry. Again, it will be important that these systems can be assembled from food-grade ingredients (preferably plant-based ones) using economic processing methods.

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