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Trends in food emulsion technology: Pickering, nano-, and double emulsions

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Natural and industrial foods are often structured materials that impart texture, flavor, visual appearance, and nutritional value to the product, such as liquid–liquid emulsions stabilized by complex interfaces. This article discusses emerging trends in food emulsion technology considering modern clean label, health, and sustainability goals. Recent scientific research has focused on Pickering emulsions, nanoemulsions, and double emulsions. Tailoring interfacial properties is essential for ensured stability of these systems. Application of green ingredients such as nanocellulose and other biopolymers is increasing in prevalence. However, interfacial characterization is specialized, expensive, and time-consuming. Microfluidic and imaging-coupled artificial intelligence methods are proposed to simplify and accelerate the characterization to food products, while nuclear magnetic resonance spectroscopy (NMR) is proposed to study the structure of multiple emulsions, facilitating the ongoing shift from largely phenomenological food emulsion approaches to interfacial engineering approaches.

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Introduction

Emulsions are prepared from two immiscible liquids by dispersing one fluid in the form of droplets in a continuous phase of the second fluid. Such systems are not thermodynamically stable and will phase-separate quickly, unless interfacially active components, such as small molecular surfactants, amphiphilic polymers, or solid particles, are added to form interfacial layers that provide kinetic stability to the formulations. Many processed foods and beverages are oil-in-water (o/w) emulsions and their shelf life often depends on their kinetic stability.

Increasing consumer awareness about safety, sustainability, and healthiness of foods has resulted in several new requirements on food and beverage products during the past decade [1]. The major consumer demands can be summarized as follows:

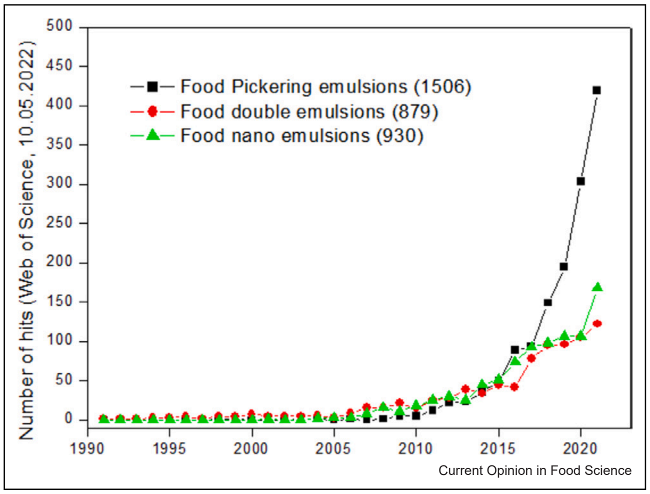
- Safe products with long shelf life and similar properties as fresh ones
- Replacement of synthetic ingredients by natural ingredients
- Fortification of food and beverages with health-related bioactive compounds

To meet these demands, there has been a tremendous interest in using Pickering emulsions, nanoemulsions, and double emulsions in food and beverage formulations (Figure 1). Here, we aim to describe the main research directions during the past 2–3 years. For each emulsion system, we identify the application areas and give examples of recent investigations. Finally, we suggest some future directions regarding characterization of the emulsion systems.

Food Pickering emulsions

Emulsions stabilized by solid particles are known as Pickering emulsions (Figure 2). Interfacial activity of a particle requires intermediate surface wettability as well as a sufficient size [2]. The particles may be organic or inorganic in nature [3,4]. Examples of organic particles include proteins, polyphenols, fat crystals, and polysaccharides such as starch, chitosan, chitin, and

Figure 1



Number of publications per year found on Web of Science (https://www.webofscience.com/wos/woscc/basic-search) using the following phrases: 'Food Pickering emulsions', 'Food double emulsions', and 'Food nano emulsions'.

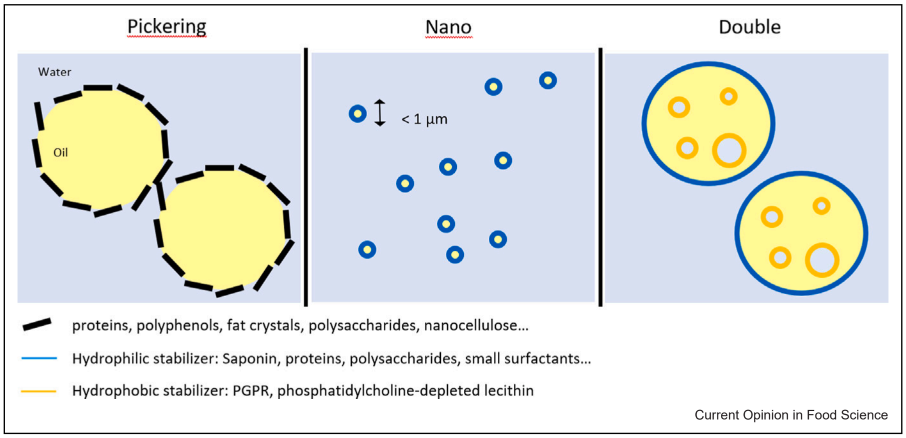
nanocellulose. Examples of inorganic particles include silica, calcium carbonate, and hydroxyapatite. Owing to a large steric barrier established by the particles at the interface, Pickering emulsions often have increased resistance against coalescence compared with emulsions stabilized by molecular surfactants.

Stability

As structuring or texturizing agents in food products, Pickering emulsions provide several advantages compared with emulsions with molecular/macromolecular surfactants. Their stability is often robust with respect to changes in physical conditions such as pH, temperature, pressure, salinity, and phase compositions, enabling simplified processing and an extended product shelf life [3]. In addition, food-grade particles are often sustainably sourced and entirely nontoxic and thereby safer than molecular surfactants that can be allergens and/or carcinogens. As such, concerted industrial efforts are underway to replace molecular surfactants with food-grade particles, improving the safety and sustainability profile of food products. A distinct emerging trend is to use nanocellulose to stabilize Pickering emulsions. For example, cellulose nanocrystals (CNCs) are known stabilizers of o/w emulsions [5], showing robust resistance against coalescence even at low interfacial CNC coverage, due to combined electrostatic and steric repulsions between droplets. In another example, stable o/w emulsions for use in mayonnaise and drinkable products are provided by combining (1) highly charged, thinly fibrillated cellulose nanofibrils (CNFs) and (2) uncharged galactoglucomannan (GGM) polysaccharides [6]. Both CNFs and GGMs contribute to interfacial stabilization, while GGM also affords oxidative resistance. It has also been shown that cellulose microfibers, along with unsaturated fatty acids, provide stable o/w emulsions, replacing unhealthy saturated fatty acids and unhealthy trans-fatty acids in food products [7]. Other current research trends include (1) engineering of electrostatic complex formation between particles and biopolymers, (2) graft modification of particles to regulate interfacial properties, and (3) engineering of depletion flocculation and depletion stabilization interactions, owing to osmotic pressure forces arising from noninteracting polymers residing in the continuous phase [4].

Numerous opportunities exist for developing Pickering emulsions by tuning the shape and surface properties (charge, grafting, complexation, etc.) of particles derived

Figure 2



Illustrations of various food emulsions.

from natural materials. Rod-like nanocelluloses provide efficient displacement of interfacial area while retaining tunable surfaces. Protein-based particles and bacterial cells are also readily modifiable. In contrast, interfacially active particles derived from synthetic materials would incur consumer resistance.

Destabilization of Pickering emulsions

In some cases, formation of Pickering emulsions may be undesirable. An example is processing of fish rest raw materials, which requires efficient oil–water separation processes. Fish protein hydrolysate is a promising nutritional product in both human and animal foods [8•]. After hydrolysis, hydrolyzed proteins become more hydrophilic than the unmodified protein. The increased hydrophilicity is attributed to amide cleavage at the C–N bond location, resulting in generation of hydrophilic carboxylic acid and hydrophilic amine functionalities. As such, hydrolysis reduces the surface activity of hydrolyzed proteins in comparison to unmodified proteins. However, hydrolyzed proteins undergo a rearrangement in comparison to the conformational state of the unmodified protein, exposing hydrophobic groups at the oil–water interface and increasing the surface activity. The size of the peptides formed is also important — small peptides are unable to stabilize emulsions. In addition, fish rest raw materials may originate from both different species and different fractions of the fish and may exist in dissimilar degradation states, altering the interfacial properties, especially with respect to the nature of the oil phase, aqueous phase, lipids, and proteins. Characterization procedures relevant to modeling oil–water separation processes include determination of (1) interfacial tension, (2) degree of hydrolysis of the protein, and (3) aqueous-phase isoelectric point. Aqueous-phase isoelectric point determination enables pH-induced protein solubilization in the aqueous phase [9], enabling rapid oil/water separation without requiring dedicated heating for viscosity reduction. Hence, for the purposes of industrial processing, rapid bulk and interfacial characterization are beneficial, necessitating implementation of high-throughput interfacial/compositional characterization as well as predictive hydrolytic modeling techniques.

Characterization

On a primary level, food Pickering emulsions are characterized in terms of particle size, particle shape, droplet size, and emulsion type (oil-in-water or water-in-oil), using microscopic techniques corroborated by macroscopic phase dispersibility observations [10•]. On a secondary level, food Pickering emulsions are characterized in terms of stability (gravitational stability, phase separation, and coalescence), bulk rheology, and interfacial tension [11].

Microfluidic methods, offering rapid analysis for small sample volumes, have been developed to determine coalescence frequencies as well as contact and film drainage times [12•] in o/w emulsions. These methods can be extended to study Pickering emulsion systems. Combined with novel artificial intelligence and deep learning-based approaches for classifying droplets [13•,14••], we believe that rapid, objective information about emulsion properties can be obtained and used to improve emulsion formulations.

Food nanoemulsions

The term nanoemulsion has emerged for the lower size range (<1000 nm) of kinetically stabilized emulsions. Nanoemulsions (Figure 2) have potential to meet several consumer demands for food and beverages. They become translucent or transparent with drop sizes smaller than 200 nm, making them attractive to use in optical transparent products such as fortified water and soft drinks. The shelf life can be prolonged by increased stability against creaming for drop sizes below 100 nm, while reduced van der Waals interactions can result in less flocculation and coalescence [15••]. However, the polydispersity index in nanoemulsions can vary from 0.1 to 0.4 [16–19], and the small droplets will be more prone to Ostwald ripening when the oil phase is somewhat water-soluble, such as flavor oils, essential oils, and short-chained triglycerides. Nanoemulsions also become more viscous than emulsions with larger drop sizes at the same oil content, paving the way for novel textural properties and low-fat foods [15••]. Finally, the high surface-to-mass ratio makes the nanoemulsions attractive carriers for bioactive compounds in functional foods [20]. However, the high surface-to-mass ratio might also require high concentrations of emulsifiers. This can make the systems costly, while the emulsifier concentrations cannot exceed the maximum permitted levels or maximum use levels defined by regulating bodies to ensure that acceptable daily intakes are not exceeded [21]. Some recent applications of nanoemulsions are listed in Table 1.

Functionalization and natural emulsifiers

Most of the recent studies on nanoemulsions are directed toward loading droplets with lipophilic bioactive compounds, typically lipids, vitamins, coloring agents, flavoring agents, and nutraceuticals (i.e. molecules that can promote health and well-being but are not critical for human health) [15••]. A variety of essential oils (i.e. flavoring agents with good antibacterial and antioxidant properties) have been used in nanoemulsions (Table 1). Furthermore, pumpkin seed oil nanoemulsions, which naturally contain bioactive carotenoids, tocopherols, and polyunsaturated fatty acids, have been prepared [17]. Lutein, an effective antioxidant, had lower bioavailability when loaded into nanoemulsions than in lipid nanoparticle systems [38], while the bioavailability was determined by the type of

Table 1

Recent examples of proposed applications and systems in food for nanoemulsions and double emulsions.

Type of emulsion	Applications/systems	Examples
Nanoemulsions	Essential oil nanoencapsulation	High citral-content essential oil from *Pectis elongata* [22]
		Oregano oil [23]
		Teucrium polium L. essential oil [24]
		Cymbopogon nardus essential oil [25]
	Edible food coatings	Red bell peppers [26]
		Tomatoes [16]
Double emulsions	Encapsulation of nutrients	Vitamins [27]
		Plant-derived pigments [28]
		β-carotene [29]
		Polyphenols [29–31]
		Soluble forms of iron [27, 32•]
	Natural stabilizers for o/w_2 interface	Arabic gum [28]
		Sodium caseinate [33,34]
		Milk protein isolate [35]
		Whey protein isolate [29,35,36]
		PPI [37]
		Lesser mealworm protein concentrate [31]

emulsifier for nanoemulsions loaded with carotene [39•]. The importance of the interfacial composition for the stability and release of bioactive compounds was clearly demonstrated by using nonionic surfactants with different hydrophilic groups to encapsulate carotene in nanoemulsions [40••].

In the quest to replace synthetic surfactants as emulsifiers, animal- and plant-based proteins as well as polysaccharides have been investigated. Whey protein isolates have been used as emulsifier in nanoemulsions [18], and compared with soybean protein isolates during encapsulation of nervonic acid [19] and carotene [39•]. Other natural emulsifiers include enzymatic peptides from cod bones [41], yolk low-density lipoproteins [42], polysaccharides [25], and polysaccharide complexes [23,43]. It is worth noticing that synthetic surfactants (typically Tweens and Spans) always must be mixed with the natural compounds to reach drop sizes below 200 nm, suggesting limited emulsifying power for many of the natural compounds.

Edible coatings

Using nanoemulsions in edible food coatings is another aspect of increasing the shelf life of food [44].

Food coatings are primarily used to limit oxidation of the food, but will also minimize loss of moisture, flavor, and odor [45]. Incorporation of nanoemulsions into edible food coatings has gained interest since it allows for the distribution of bioactive compounds in the materials. Typically, nanoemulsions are added to solutions of chitosan, carboxymethyl cellulose, or gelatin, and subsequently casted into films. Edible coatings have been studied for various foods (Table 1).

Characterization

Drop size and polydispersity measurements from dynamic light scattering are constantly used to evaluate the stability of nanoemulsions over time, and often under external stresses (heat-cooling cycles, varying salinity, and pH). Light transmission profiles, collected along the entire sample in centrifugal fields, have also been used in stability studies. The morphology of droplets, location and state of encapsulated compounds, and quantification of the loading capacity of bioactive compounds are also typically determined. The release of encapsulated ingredient is generally studied by conducting in vitro digestion experiments of the emulsions, for instance, to follow the free fatty acid released from triglyceride oil droplets [43], and determining the bioaccessibility of the encapsulated ingredients [15••,39•,43]. Notably, the interfacial layers constitute a considerable part of the dispersed droplets in nanoemulsions. Despite of this, there are surprisingly few studies that characterize interfacial properties and effects. The interfacial tension of natural surfactants has been measured to evaluate their emulsifying capacity, while interfacial tension and interfacial dilatation measurements have been used to follow alterations of interfacial properties during simulated digestive conditions [18,46]. Nevertheless, the importance of the interfacial composition on the stability and release of bioactive compounds has been clearly demonstrated [39•,40••], and we believe that improved knowledge of interfacial layers and their interactions with bioactive compounds has large potential to improve formulation and performance of functional nanoemulsions.

Food double emulsions

Double emulsions (Figure 2) are composed of droplets dispersed in other droplets, and water-in-oil-in-water (w_1/o/w_2) emulsions with different aqueous compositions are mostly encountered in foods. The systems are normally prepared by emulsifying a premade w_1/o emulsion into the w_2 phase. If the w_1/o emulsion has drop sizes in the submicrometer range, they are also referred to as nanoemulsions.

The growing interest in double emulsions is mostly linked to their use in fortified and healthier foods, comprising fat-reduced emulsions where oil droplets are replaced by w_1/o emulsions [47], and nutrients are encapsulated to protect them from degradation and control the kinetics of their release during ingestion (see Table 1 for different nutrients). The encapsulation of concentrated sucrose solutions to increase the perception of sweetness has also been studied [48].

Preparation and stability control

The stability control of double emulsions is substantially more difficult than for single emulsions. This is due to the osmotic pressure difference between the two aqueous phases and the need for at least two emulsifiers with different hydrophilic–lipophilic balance to stabilize the different oil–water interfaces.

Polyglycerol ester of polyricinoleic acid efficiently reduces oil–water interfacial tension and provides good stabilization of water droplets [49]. It is considered a safe substance [50], and is the most common hydrophobic emulsifier for w_1/o emulsions [28,29,32•,33,35–37,47,48,51–53]. Its only identified drawback is a potential unpleasant taste [54]. Phosphatidylcholine-depleted lecithin, known to stabilize w/o emulsions, can be an alternative emulsifier in double emulsions [55•]. Another alternative is the stabilization of water droplets by fat crystals (i.e. Pickering emulsions) [56].

The hydrophilic emulsifiers for the o/w_2 interface are more diverse. Small synthetic surfactants such as Tween 80 and 60 are still used [30,33], while polysaccharides and proteins are predominant due to less migration from the outer to inner droplets and their ability to form viscoelastic layers [54]. It has, for example, been shown that pea protein isolate (PPI) and octenyl succinic anhydride (OSA) starch were more efficient than Tween 20 in stabilizing $w_1/o/w_2$ emulsions [37]. Other natural stabilizers are listed in Table 1. Furthermore, natural products can be modified to increase interfacial activity/stabilizing properties, such as OSA-modified starch [48], protein–carbohydrate complexes [52], and saponin–chitosan double-layer coatings [32•]. Finally, particles such as octenylsuccinate quinoa starch [57] can be implemented to stabilize external oil droplets forming Pickering emulsions.

Another strategy to increase the stability of multiple emulsion is to jellify the inner water droplets. Natural gelling agents include whey proteins and egg white [51], carrageenan [53], whey protein isolate [58], and pectin [34,58]. Oleogelation of the oil phase has also been reported [29], but a crystalline oil phase in $w_1/o/w_2$ also leads to increased emulsion viscosity [28].

The balance of the osmotic pressure in the aqueous phases with the Laplace pressure is a final aspect of stability control in double emulsions achieved by adding salts or sugar to the aqueous phases [59].

Characterization

Most of the techniques used to characterize single emulsions are also implemented for multiple emulsions [60•]. Optical, fluorescence, and laser scanning confocal microscopies [30–32•,52] have been used to analyze the presence and structure of multiple emulsions. The droplet-size distributions (DSD) of outer droplets are generally measured by static laser diffraction [30,31,47,53], while the detection of inner droplet sizes is more difficult. Typically, it is measured after the initial emulsification step by microscopy or light scattering techniques [34,47]. However, the inner droplet size can change during the 2nd emulsification step, and techniques for determining DSD of inner droplets in the double emulsions are desirable.

Nuclear magnetic resonance (NMR) spectroscopy is a promising technique for probing the inner droplet size, and various approaches have been implemented to determine inner droplet sizes and molecular exchange between aqueous phases in double emulsions [61]. New low-field NMR procedures for simple emulsions acquire data more rapidly and have eliminated the need to presuppose the shape of the DSD [62]. We believe that these approaches can be implemented in DSD and stability measurements in double emulsions as well.

The study of the behavior and release of encapsulated ingredient in the human body generally starts by the determination of encapsulation efficiency [28,31,32•], that is, the proportion of this ingredient still present in the W_1 droplets after preparation of the double emulsions. The in vitro digestion behavior of double emulsions can be determined by observing the double-emulsion aspect and properties under digestion conditions [30,35]. The bioaccessibility of the encapsulated ingredient (for instance, proanthocyanidins and β-carotene [29]) can also be determined in vitro. In addition, the cytotoxicology of double emulsions can be assessed in vitro [30].

It is only by combining and developing these multiple advanced characterization techniques to understand the complex destabilization pattern and the properties (release of the encapsulated ingredient…) of double emulsions that the efficient commercial product could be designed in economic ways.

Conclusion

Emerging trends in food emulsions are an R&D focus on Pickering emulsions, multiple emulsions, and nanoemulsions. Proper characterization of both interfacial properties and dispersion behavior is the key to achieve commercial products for all these systems.

Low-field NMR is an applicable technique to investigate the structure of multiple emulsions as well as nanoemulsions, and is applicable to opaque samples.

Microfluidic characterization coupled to digital imaging artificial intelligence methods has recently emerged with capabilities to rapidly characterize coalescence rates in emulsion systems. Such techniques may enable rapid screening and interfacial characterization of emulsions prepared with green and sustainable emulsifying agents, whether in molecular or particle form, replacing current synthetic food-grade surfactants. Microfluidic platforms may facilitate interfacial rheological measurements, further supporting the rapid measurement and prediction of food emulsion stability.

Conflict of interest statement

The authors have no conflict of interest to declare.

Data Availability

No data were used for the research described in the article.

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