Emulsion Design to Improve the Delivery of Functional Lipophilic Components

David Julian McClements

Department of Food Science, University of Massachusetts, Amherst, Massachusetts 01003;
email: mcclements@foodsci.umass.edu

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Abstract

The food industry has used emulsion science and technology for many years to create a diverse range of food products, such as milk, cream, soft drinks, nutritional beverages, dressings, mayonnaise, sauces, dips, deserts, ice cream, margarine, and butter. The majority of these food products are conventional oil-in-water (O/W) or water-in-oil (W/O) type emulsions. Recently, there has been increasing interest within the food industry in either improving or extending the functional performance of foods using novel structured emulsions. This article reviews recent developments in the creation of structured emulsions that could be used by the food and other industries, including nanoemulsions, multiple emulsions, multilayer emulsions, solid lipid particles, and filled hydrogel particles. These structured emulsions can be produced from food-grade [generally recognized as safe (GRAS)] ingredients (e.g., lipids, proteins, polysaccharides, surfactants, and minerals), using simple processing operations (e.g., mixing, homogenizing, and thermal processing). The structure, production, performance, and potential applications of each type of structured emulsion system are discussed.

INTRODUCTION

The food industry currently relies on the principles of emulsion science and technology to create a wide variety of different food products, including milk, cream, coffee creamer, soft drinks, nutritional beverages, sauces, dips, deserts, dressings, mayonnaise, ice cream, margarine, and butter (Dickinson 1992, Friberg et al. 2004, McClements 2005a). These products may be in an emulsified state in their final form (e.g., milk or cream) or they may have been in an emulsified state sometime during their manufacture (e.g., powdered soup, sauce, or coffee creamer). There are two major categories of conventional food emulsions currently utilized by the food industry: oil-in-water (O/W) and water-in-oil (W/O). O/W emulsions consist of oil droplets dispersed in an aqueous medium (e.g., milk, cream, beverages, and dressings), whereas W/O emulsions consist of water droplets dispersed in an oily medium (e.g., margarine and butter). The food manufacturer can control the physicochemical and sensory properties of these products (e.g., shelf life, appearance, texture, and flavor) by careful selection of the ingredients and processing operations used to manufacture them (McClements 2005a). Knowledge of emulsion science and technology aids in the efficient design and production of these types of products. In particular, emulsion science provides a fundamental understanding of the relationship between the properties of the droplets within an emulsion (e.g., concentration, size, charge, physical state, interfacial characteristics, and interactions) and its physicochemical properties (e.g., stability, optical properties, rheology, and molecular distribution). Recently, there has been a trend toward the development of structured emulsion systems that are more sophisticated than conventional O/W or W/O emulsions, e.g., nanoemulsions, multiple emulsions, multilayer emulsions, solid lipid nanoparticles, and filled hydrogel particles. These emulsions may have novel applications within the food industry for modifying emulsion properties or for engineering novel performance. This review article describes how these novel structured emulsions can be produced, highlights their properties, and discusses their potential applications. Before discussing structured emulsions, it is useful to begin with a brief overview of emulsion science and technology in general, focusing on the relationship between droplet characteristics and macroscopic emulsion properties.

This article concentrates on structured emulsions whose continuous phase is aqueous (i.e., O/W, W/O/W, W/W or O/W/W), given that these currently have the greatest potential for utilization within the food and other industries. In addition, the article focuses primarily on liquid systems, rather than dried systems, and so does not consider microencapsulation by drying, which has been reviewed elsewhere (Madene et al. 2006, Desai & Park 2005, Vega & Roos 2006).

EMULSION SCIENCE AND TECHNOLOGY

Generally, an emulsion consists of at least two immiscible liquids (usually oil and water, but not always), with one of the liquids being dispersed as small spherical droplets in the other (Friberg et al. 2004, McClements 2005a, Dickinson 1992, Dickinson & Stainsby 1982). A number of different terms are in common usage to describe different kinds of emulsions, and it is important to clarify what these terms actually mean (**Table 1**). A conventional emulsion, also known as a macroemulsion, typically has droplets with mean diameters between 100 nm and 100 μm. This type of emulsion is thermodynamically unstable and tends to be optically turbid or opaque because the droplets have a size similar to the wavelength of light ($d \approx \lambda$) and so strongly scatter light (provided the refractive index contrast is not close to zero). A nanoemulsion can be considered to be a conventional emulsion that contains very small droplets, i.e., mean diameters between 20 nm and 100 nm (Tadros et al. 2004). The relatively small size of the droplets compared with the wavelength of light ($d < \lambda$) means that they tend to be transparent or only slightly turbid

Table 1 Properties of different types of emulsions prepared from water and oil phases

Emulsion type	Diameter range	Thermodynamic stability	Surface-to-mass ratio (m^2/g)	Appearance
Macroemulsion	0.1–100 μm	Unstable	0.07–70	Turbid/opaque
Nanoemulsion	20–100 nm	Unstable	70–330	Transparent
Microemulsion	5–50 nm	Stable	130–1300	Transparent

(as with microemulsions). In addition, the small droplet size means that they have much better stability to gravitational separation and aggregation than conventional emulsions (Tadros et al. 2004, Wooster et al. 2008). On the other hand, these systems are still thermodynamically unstable systems because the separate oil and water phases have a lower free energy than the emulsified oil and water phases (as with conventional emulsions). A microemulsion is a thermodynamically stable system (i.e., it forms spontaneously given sufficient time) that typically contains particles with diameters somewhere in the 5 nm to 50 nm range. For this reason, microemulsions are usually optically transparent because the particle size is much smaller than the wavelength of light ($d < \lambda$), so that light scattering is weak. In the remainder of this article, the term emulsion is used to refer to thermodynamically unstable systems (conventional emulsions and nanoemulsions).

Emulsions are typically classified according to the spatial distribution of the oil and water phases relative to each other. A system that consists of oil droplets dispersed within a watery phase is called an oil-in-water (O/W) emulsion, whereas a system that consists of water droplets dispersed in an oily phase is called a water-in-oil (W/O) emulsion. The liquid that makes up the droplets is usually referred to as the dispersed or discontinuous phase, whereas the surrounding liquid is referred to as the dispersing or continuous phase. As mentioned above, it is also possible to prepare various types of multiple emulsions, e.g., oil-in-water-in-oil (O/W/O) or water-in-oil-in-water (W/O/W) emulsions (Benichou et al. 2004a, van der Graaf et al. 2005, Garti & Bisperink 1998, Muschiolik 2007). It is also possible to form emulsions based on the thermodynamic incompatibility of mixed biopolymer solutions, e.g., water-in-water (W/W) or oil-in-water-in-water (O/W/W) emulsions (Kim et al. 2006, Norton & Frith 2001, Norton et al. 2006). All these types of emulsions are thermodynamically unfavorable systems that tend to break down over time, e.g., owing to gravitational separation, flocculation, coalescence, partial coalescence, and/or Ostwald ripening (Friberg et al. 2004, McClements 2005a, Dickinson 1992). A great deal of emulsion science and technology is therefore concerned with the creation of emulsions that have a sufficiently long kinetic stability. In the food industry, kinetic stability is usually engineered into products by incorporating substances known as stabilizers, e.g., emulsifiers, texture modifiers, weighting agents, and ripening retarders.

- Emulsifier: An emulsifier is a surface-active molecule that adsorbs to the surface of the droplets formed during homogenization. Its purpose is to facilitate droplet disruption in the homogenizer and to stabilize the droplets formed against aggregation.
- Texture modifier*:* A texture modifier is a substance that thickens or gels the continuous phase. Its purpose is to improve emulsion stability by retarding or preventing droplet movement.
- Weighting agent*:* A weighting agent is a substance that is added to the droplets to match their density to the surrounding continuous phase. Its purpose is to reduce the driving force for gravitational separation and therefore prevent or retard creaming or sedimentation.
- Ripening retarder*:* A ripening retarder is a highly hydrophobic material that is added to lipid droplets to slow down or prevent Ostwald ripening.

The selection of the most appropriate stabilizer(s) to use in an emulsion is one of the most important things that a food manufacturer can do to control the shelf life and physicochemical properties of food products. The other major factor that food manufacturers can use to control the properties of the final product is to carefully select the most appropriate processing operations, e.g., order of addition, homogenization, shearing conditions, temperature profile, etc. (McClements 2005a). In the remainder of this section emulsion droplet properties are discussed, and then their relationship to the bulk physicochemical properties of emulsions is highlighted. This information is provided because it helps to understand how structuring the particles in emulsions can be used to alter their physicochemical properties, stability, and performance.

Particle Characteristics

The physicochemical properties of emulsions, such as their rheology, optical properties, stability, molecular partitioning, and release characteristics, are mainly determined by the characteristics of the droplets that they contain (McClements 2005a).

Particle concentration. The droplet concentration is usually expressed as the number, mass, or volume of droplets per unit volume or mass of emulsion (McClements 2005a). For example, the disperse phase volume fraction (ϕ) is the volume of droplets per unit volume of emulsion. The droplet concentration of an emulsion can usually be controlled by varying the proportions of the two immiscible liquids used to prepare it. Alternatively, an emulsion may be prepared with a particular droplet concentration and then be either diluted (e.g., by adding more continuous phase) or concentrated (e.g., by gravitational separation, filtration, or centrifugation). Consequently, a food manufacturer normally has good control over the droplet concentration in a prepared emulsion.

Particle size distribution. The particle size distribution (PSD) of an emulsion represents the fraction of particles within different size classes (McClements 2005a). A PSD is typically presented in a tabular form or as a plot of particle concentration (e.g., volume or number percent) versus droplet size (e.g., diameter or radius). It is often convenient to represent a PSD of an emulsion by a measure of the central tendency (e.g., mean, median, or modal) and a measure of the width of the distribution (e.g., standard deviation). The PSD of an emulsion can usually be controlled by varying homogenization conditions (e.g., intensity or duration of energy input) or system composition (e.g., the type and concentration of emulsifier used or the viscosity ratio of the disperse and continuous phases) (McClements 2005a). Smaller droplets can usually be produced by increasing the intensity or duration of homogenization or by increasing the concentration of emulsifier used (Schubert & Engel 2004, Walstra 1993, Wooster et al. 2008).

Particle charge. The droplets in emulsions often have an electrical charge, which plays an important role in their functional performance and stability. The electrical properties of a droplet are usually characterized in terms of its surface charge density (σ), surface potential (Ψ_0), and/or zeta (ζ)–potential (Hunter 1986). The surface charge density is the number of unit electrical charges per unit surface area. The surface electrical potential is the free energy required to increase the surface charge density from zero to σ by bringing charges from an infinite distance to the surface through the surrounding medium. The surface electrical potential depends on the ionic composition of the surrounding medium due to electrostatic screening effects and usually decreases as the ionic strength of the aqueous phase increases. The ζ-potential is the electrical potential at the shear plane, which is defined as the distance away from the droplet surface below which the counter-ions remain strongly attached to the droplet when it moves in an electrical field. Practically, the ζ-potential is often a better representation of the electrical characteristics of an emulsion droplet than the surface potential because it inherently accounts for the adsorption of any charged counter-ions. In addition, the ζ-potential is much easier to measure than the surface potential or charge density, and therefore droplet charges are usually characterized in terms of ζ-potential (Hunter 1986). The electrical characteristics of emulsion droplets can be controlled by careful selection of particular emulsifier types. Droplets stabilized by nonionic surfactants tend to only have a small droplet charge (e.g., Tweens and Spans), those stabilized by anionic surfactants have a negative charge (e.g., lecithin, DATEM, CITREM, fatty acids), those stabilized by cationic surfactants have a positive charge (e.g., lauric arginate), those stabilized by polysaccharide emulsifiers tend to have a negative charge (e.g., gum Arabic, modified starch, and beet pectin), and those stabilized by proteins have a positive charge below the isoelectric point (pI) and negative charge above it (e.g., whey protein, casein, soy proteins, egg proteins). The charge on emulsifier-coated droplets may also be altered by adsorption of other charged substances onto their surfaces, such as proteins, polysaccharides, or multivalent ions (McClements 2005a).

Interfacial characteristics. The droplets in most emulsions are coated by a layer of adsorbed species in order to protect them from aggregation (e.g., emulsifiers or biopolymers). The properties of the interfacial region are determined by the type, concentration, and interactions of any surface-active species present during homogenization as well as by the events that occur before, during, and after emulsion formation, e.g., denaturation, complexation, competitive adsorption, layer-by-layer formation (Dickinson 2003, Guzey & McClements 2006a). It is sometimes possible to control the characteristics of the interfacial layer, such as tension, charge, thickness, permeability, rheology, and environmental responsiveness, by altering system composition or processing conditions. Controlling the interfacial characteristics is one of the most powerful methods of designing structured systems with specific functional performances. The interfacial characteristics of emulsion droplets can be controlled by selection of specific emulsifier types. For example, caseinates tend to form thick fluid-like interfacial layers, whereas whey proteins form thin elastic-like layers (Dickinson 1992, Dickinson 2003). Depositing successive layers of charged biopolymers onto oppositely charged lipid droplets can be used to form nano-laminated coatings with different thicknesses or charges around the droplets (Guzey & McClements 2006a).

Particle physical state. By definition, the droplets that make up the dispersed phase of a conventional emulsion are liquid, but in some emulsion-like systems they are either partially or fully solidified, e.g., solid lipid particles (McClements 2005a, Walstra 2003, Muller & Keck 2004, Wissing et al. 2004). For example, the oil droplets in an O/W emulsion can be made to crystallize by reducing the temperature sufficiently below the melting point of the oil phase. It should be noted that the crystallization temperature may be appreciably less in an emulsified fat than a bulk fat because of supercooling effects. In addition, the nature of the crystals formed by an emulsified fat may be different from those formed by a bulk fat because of curvature affects and the limited volume present in an individual emulsion droplet, e.g., crystal structure, dimensions, and melting behavior (Muller & Keck 2004, Wissing et al. 2004). The concentration, nature, and location of the fat crystals within the lipid droplets in an O/W emulsion can be controlled by careful selection of oil type (e.g., solid fat content versus temperature profile), thermal history (e.g., temperature versus time), emulsifier type (e.g., tail group characteristics) and droplet size (Walstra 2003, Muller & Keck 2004, Muller et al. 2000).

Physicochemical Properties of Emulsions

The properties of the emulsion droplets mentioned above ultimately determine the bulk physicochemical properties of the final product, e.g., optical properties, rheology, stability, flavor, or release characteristics.

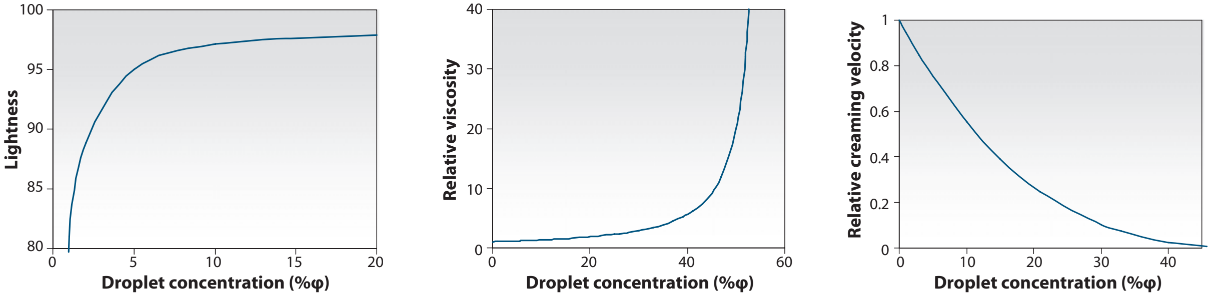

Figure 1

Dependence of emulsion lightness, viscosity, and creaming stability on droplet concentration.

Optical properties. The optical properties of an emulsion-based product determine its overall appearance and therefore its consumer desirability. The optical properties of emulsions are mainly determined by their opacity and color, which can be quantitatively described using tristimulus color coordinates, such as the $L^*a^*b^*$ system (McClements 2002b, 2005a). In this color system, L^* represents the lightness, and a^* and b^* are color coordinates, where $+a^*$ is the red direction, $-a^*$ is the green direction; $+b^*$ is the yellow direction, $-b^*$ is the blue direction; low L^* is dark, high L^* is light. The opacity of an emulsion can therefore be characterized by the lightness (L^*), whereas the color intensity can be characterized by the chroma: $C = (a^{*2} + b^{*2})^{1/2}$. The optical properties of emulsions are mainly determined by the relative refractive index, the droplet concentration, and the droplet size (McClements 2002a,b; 2005a). The lightness of an emulsion tends to increase with increasing refractive index contrast and with increasing droplet concentration, and it has a maximum value at a droplet size where light scattering is strongest (i.e., $d \approx \lambda$). The color intensity is usually inversely related to the lightness, i.e., when the lightness increases, the chroma decreases. Thus, at a constant dye concentration the color of an emulsion tends to fade as its lightness increases. For O/W emulsions, the lightness increases steeply as the lipid droplet concentration is increased from 0 wt% to 5 wt% but then increases more gradually at higher droplet concentrations (**Figure 1**). The impact of the droplet characteristics on the overall appearance of an emulsion may be an important consideration when designing specific food products. Some food products are transparent or only slightly turbid (e.g., soft drinks and fruit beverages) and so the droplets should not cause a large increase in opacity. In this kind of system, it may be useful to use microemulsions or nanoemulsions that have very small droplets that do not scatter light strongly. Other food products are optically opaque (e.g., dressings, sauces, mayonnaise) and therefore the opacity produced by the droplets may be less important, so that conventional emulsions that do scatter light appreciably can be used. The particles in structured emulsions may have relatively complex structures compared with simple spherical lipid droplets, which will impact their interactions with light waves. For example, lipid droplets may be embedded within biopolymer particles (filled hydrogel particles), or lipid droplets may contain water droplet inclusions (multiple emulsions), which will alter their size, shape, and refractive index.

Rheology. Depending on their composition, structure, and droplet interactions, emulsions can exhibit a wide variety of different rheological characteristics: viscous liquids, viscoelastic liquids, viscoelastic solids, plastics, or elastic solids (Walstra 2003, McClements 2005a, Genovese et al. 2007). The rheology of relatively dilute emulsions is usually characterized in terms of their shear viscosity. The shear viscosity of an emulsion is determined primarily by the continuous phase viscosity (η_C), the droplet concentration (ϕ), and the nature of the droplet-droplet interactions (w): $\eta = \eta_C \times f(\phi, w)$ (McClements 2005a, Genovese et al. 2007).

The viscosity of an emulsion tends to increase with increasing droplet concentration, gradually at first and then steeply as the droplets become more closely packed (**Figure 1**). Around and above the droplet concentration at which close packing occurs (typically around 40–60% for a nonflocculated emulsion), the emulsion exhibits solid-like characteristics such as visco-elasticity and plasticity (McClements 2005a). The droplet concentration at which the steep increase in emulsion viscosity is observed depends on the nature of the droplet interactions in the system, decreasing for either strong attractive or strong repulsive interactions (McClements 2005a). The viscosity of an emulsion tends to increase when the droplets are flocculated because the effective particle concentration is increased as a result of the continuous phase trapped within the floc structure. In addition, shear thinning behavior is observed in flocculated emulsions because of deformation and breakdown of the floc structure as shear stresses increase. The impact of the droplet characteristics on the overall rheology of an emulsion may be an important consideration when designing food products. Some foods have a relatively low viscosity (such as beverages) and so the droplets present should not appreciably increase the overall viscosity. Other foods are highly viscous or gel-like (e.g., dressings, dips, desserts), and the droplets present may contribute to the overall viscosity or gel network formation. In structured emulsions, the particles may have relatively complex structures rather than being simple spherical droplets, which may impact the rheology of the overall system. For example, lipid droplets may be embedded within biopolymer particles (filled hydrogel particles) or lipid droplets may contain water droplet inclusions (multiple emulsions), so that the effective particle concentration is appreciably bigger than the lipid concentration. Structured emulsions may contain particles that have a higher effective volume fraction than the lipid phase itself, leading to considerably higher viscosities at the same lipid concentration.

Stability. Emulsions are thermodynamically unfavorable systems that tend to break down over time as a result of a variety of physicochemical mechanisms (**Figure 2**), including gravitational separation, flocculation, coalescence, and Ostwald ripening (Friberg et al. 2004, McClements 2005a, Dickinson 1992). Gravitational separation is one of the most common forms of instability in emulsions, and may take the form of either creaming or sedimentation, depending on the relative densities of the dispersed and continuous phases. Creaming is the upward movement of droplets due to the fact that they have a lower density than the surrounding liquid, whereas sedimentation is the downward movement of droplets due to the fact that they have a higher density than the surrounding liquid. Liquid edible oils normally have lower densities than liquid water and so creaming is more prevalent in oil-in-water emulsions, whereas sedimentation is more prevalent in water-in-oil emulsions. Nevertheless, this may not be the case in emulsions that contain fully or partially crystalline lipids because the density of oils usually increases when crystallization occurs. In addition, in structured emulsions the lipid droplets may be surrounded by dense biopolymer coatings (multilayer emulsions) or embedded in dense biopolymer particles (filled biopolymer particles), which may impact their tendency to cream or sediment.

Molecular distribution and release characteristics. The ability of emulsions to incorporate and/or release functional molecules, such as flavors, antimicrobials, and nutraceuticals, depends strongly on their composition and microstructure, given that these factors determine equilibrium partition coefficients and molecular transport kinetics (McClements 2005a). For example, an emulsion system may be used as a carrier for lipophilic flavor molecules that need to be released in the mouth during consumption. The perception of flavor molecules within an emulsion depends strongly on its composition, e.g., the polarity, concentration, dimensions, and physical state of the

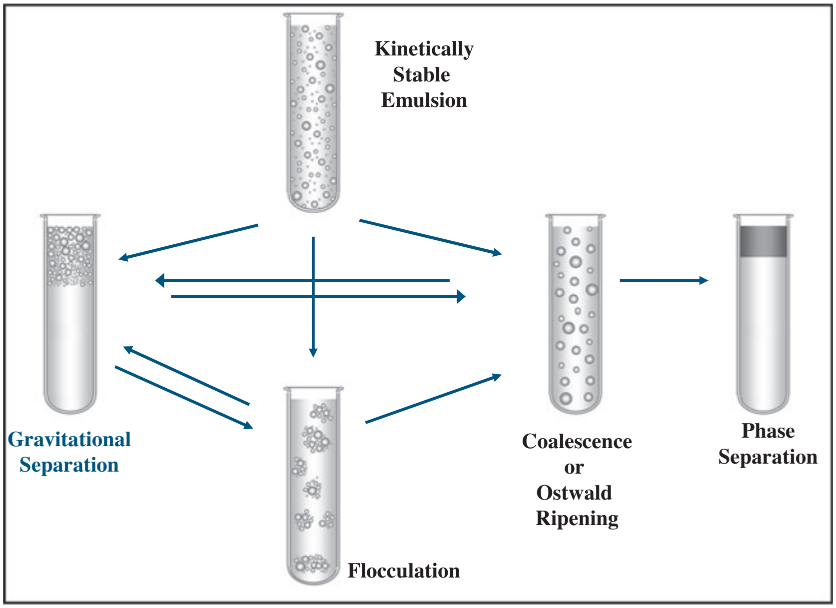

Figure 2

Schematic diagram of most common instability mechanisms that occur in food emulsions: creaming, sedimentation, flocculation, coalescence, Ostwald ripening, and phase inversion.

lipid phase present. The initial concentration of nonpolar molecules in the headspace of an emulsion decreases as the lipid concentration increases, thereby reducing the perceived flavor intensity. The release profile of nonpolar flavor molecules from emulsions is also strongly dependent on lipid concentration: A high fat product tends to give a sustained release, whereas a low-fat product gives an intense burst. Obviously, these factors are important when designing emulsion systems with specific attributes. Another important physicochemical property of emulsion systems is their ability to release encapsulated functional components. In particular, it is important to establish any potential trigger mechanisms for release (e.g., pH, ionic strength, temperature, enzymes, etc.) as well as the rate and extent of release. In an emulsion, release is usually characterized in terms of the increase in concentration of the encapsulated compound in the continuous phase or in some target material (such as the mouth, nose, stomach, or gastrointestinal tract) as a function of time. A number of parameters can be derived from such curves, such as the area below the curve (AUC), the maximal concentration released (C_{max}), and the time to reach the maximum concentration (t_{max}) (Aguilera 2006). The release rate of encapsulated components from within emulsions depends on many factors, including their equilibrium partition coefficients, their original location, the mass transfer coefficients of the components in the different phases, mechanical agitation, and the microstructure of the system, e.g., droplet size and layer thickness (McClements 2005a). Consequently, it is possible to structurally design emulsion-based systems that are capable of controlling the release of encapsulated components by selecting appropriate ingredients and microstructures (Lian et al. 2004).

STRUCTURAL DESIGN OF EMULSIONS

In this section, a brief overview of the major kinds of structured emulsions that can be created from food-grade components is given. The primary focus will be on emulsion-based systems

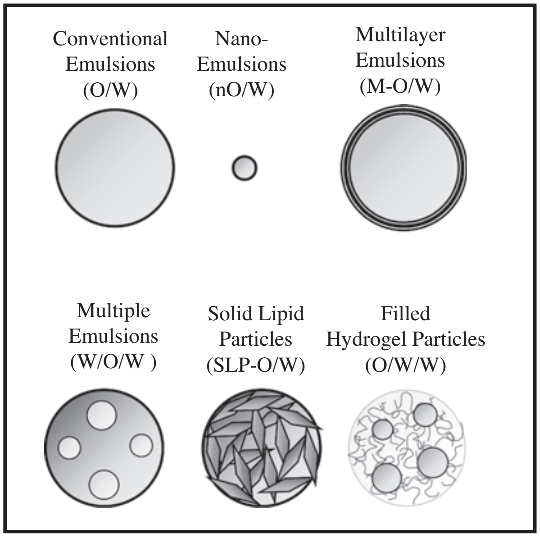

Figure 3

Examples of different kinds of structured emulsion systems that can be designed using food-grade ingredients. These include conventional emulsions, nanoemulsions, multilayer emulsions, multiple emulsions, solid lipid nanoparticles and filled hydrogel particles.

that are dispersible in aqueous solutions, i.e., those in which water is the continuous phase. In addition, only emulsion systems (thermodynamically unstable), and not microemulsion systems (thermodynamically stable), are considered.

Conventional Emulsions

Conventional O/W emulsions consist of oil droplets dispersed in an aqueous continuous phase, with the oil droplets being surrounded by a thin interfacial layer consisting of a single laye of emulsifier molecules (**Figure 3**) (Friberg et al. 2004, McClements 2005a, Dickinson 1992). They are the most common form of emulsion currently used in the food industry and are found in a variety of food products, including milk, cream, beverages, dressings, mayonnaise, dips, sauces, and deserts.

Structure and properties. The concentration and particle size distribution of the oil droplets in conventional O/W emulsions can be controlled, as can the nature of the emulsifier used to stabilize the system. The oil droplets in most food emulsions typically have diameters somewhere between 100 nm and 100 μm, although larger and smaller droplets are possible in certain applications. The interfacial layer is typically between approximately 1 nm and 10 nm thick for food-grade emulsifiers (e.g., surfactants, phospholipids, proteins, or polysaccharides), but it may be appreciably thicker if biopolymer multilayers are formed around the droplets (Guzey & McClements 2007). The electrical charge on the droplets can be controlled by selecting an appropriately charged emulsifier, which may be positive, noncharged, or negative.

Conventional emulsions tend to be cloudy or opaque in appearance because the dimensions of the lipid droplets are on the same order as the wavelength of light ($d \approx \lambda$) so that light scattering is relatively strong. The lightness of these emulsions tends to increase with increasing droplet concentration and increasing refractive index contrast and has a maximum value at a

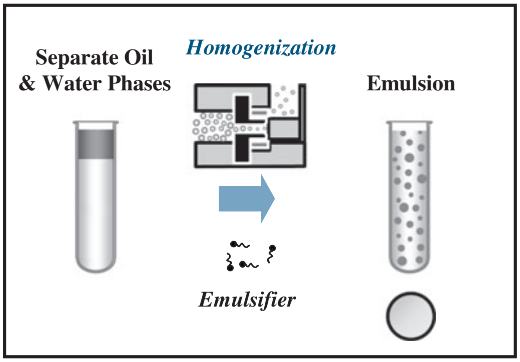

Figure 4

Oil-in-water emulsions are conventionally produced by homogenizing an oil phase and aqueous phase together in the presence of a water-soluble emulsifier.

particular particle diameter ($d \approx 200$ nm). The rheology of conventional emulsions varies from low-viscosity liquids at low droplet concentrations (e.g., milk), to high-viscosity liquids at intermediate droplet concentrations (e.g., cream), to semisolids at high droplet concentrations (e.g., mayonnaise). The viscosity of the emulsions may increase appreciably if the droplets are flocculated or a thickening agent is added to the aqueous phase. Conventional emulsions are particularly prone to gravitational separation and droplet aggregation because of the relatively large size of the droplets. The release characteristics of conventional emulsions can be controlled by varying the dimensions of the droplets, with the release rate increasing with decreasing droplet diameter (McClements 2005a).

Preparation procedures. Conventionally, oil-in-water (O/W) emulsions are prepared by homogenizing an oil phase and an aqueous phase together in the presence of a water-soluble emulsifier (**Figure 4**). A variety of different homogenizers are available, including high-shear mixers, high-pressure homogenizers, colloid mills, ultrasonic homogenizers, and membrane homogenizers (McClements 2005a; Walstra 1993, 2003). The choice of a particular kind of homogenizer, and of the operating conditions used, depends on the characteristics of the materials being homogenized (e.g., viscosity, interfacial tension, shear sensitivity) and of the required final properties of the emulsion (e.g., droplet concentration, droplet size, viscosity). For example, the size of the droplets in an O/W emulsion produced by a high-pressure homogenizer can usually be decreased by increasing the homogenizer pressure or number of passes. Non-polar functional ingredients are normally dispersed in the oil phase prior to homogenization with the water phase. If the functional component was crystalline (e.g., phytosterols or carotenoids), then it may be necessary to ensure that it is used at a level below its saturation concentration in the carrier oil, or to warm the lipid phase prior to homogenization to melt any crystals present (given that fat crystals can cause fouling of homogenizers). If the functional component was susceptible to chemical degradation (e.g., ω-3 fatty acids, CLA, and carotenoids), then it may be necessary to carefully control homogenization conditions to avoid exposure to factors that increase the degradation rate, e.g., high temperatures, oxygen, light, or transition metals.

Potential advantages and limitations. In this section, we summarize the potential advantages and disadvantages of using conventional emulsions within the food industry.

Potential advantages.

- They are relatively easy and inexpensive to prepare compared with other types of emulsion-based systems.
- They are useful when cloudiness or creaminess is required in a product.

Potential disadvantages.

- They are optically opaque and therefore cannot be used in systems in which optical clarity is required.
- There are only a limited number of food-grade emulsifiers available to stabilize conventional emulsions, which limits the potential for engineering novel or improved functional performance into products.
- They are often prone to physical instability (e.g., gravitational separation, flocculation, coalescence), especially when exposed to environmental stresses such as heating, chilling, freezing, drying, pH extremes, and high mineral concentrations.
- There is limited ability to protect and control the release of functional components because the small size of the droplets (~μm) and the interfacial layers (~nm) means that the time scales for molecular diffusion of substances are extremely short.

Nanoemulsions

As with conventional emulsions, O/W nanoemulsions also consist of oil droplets dispersed within an aqueous continuous phase, with each oil droplet being surrounded by a thin interfacial layer consisting of emulsifier molecules (**Figure 3**) (Tadros et al. 2004). However, the diameter of the droplets in nanoemulsions (20–100 nm) is considerably smaller than that in conventional emulsions (100 nm – 100 μm).

Structure and properties. The concentration and particle size distribution of the oil droplets in nanoemulsions can be controlled, as can the nature of the emulsifier used to stabilize the system. The electrical charge on the nanodroplets can also be controlled by selecting an appropriately charged emulsifier, which may be positive, neutral, or negative.

Nanoemulsions tend to be transparent in appearance because the dimensions of the lipid droplets are much smaller than the wavelength of light ($d \ll \lambda$), causing light scattering to be relatively weak. Nevertheless, they may become turbid or opaque if droplet growth occurs during storage. The rheological properties of nanoemulsions follow similar trends to conventional emulsions, i.e., the viscosity increases with increasing droplet concentration. Nevertheless, the viscosity of a nanoemulsion may be appreciably greater than that of a conventional emulsion at the same lipid concentration if it contains a thick or electrically charged interfacial layer that increases droplet-droplet repulsion (Weiss & McClements 2000, Tadros et al. 2004). Nanoemulsions are usually highly stable to gravitational separation because the relatively small droplet size means that Brownian motion effects dominate gravitational forces (McClements 2005a). Nanoemulsions also have good stability against droplet aggregation because the strength of the net attractive forces acting between droplets usually decreases with decreasing droplet size (McClements 2005a). The fact that the droplets are very small in nanoemulsions means that any encapsulated material usually diffuses out of them very quickly. In addition, they have a very high surface area-to-volume ratio, so any chemical reactions that occur at the oil-water interface should be accelerated, e.g., lipid digestion.

Preparation procedures. As with conventional emulsions, nanoemulsions are usually prepared by homogenizing an oil phase and an aqueous phase together in the presence of a water-soluble emulsifier (**Figure 4**). Nevertheless, a number of special considerations must be taken into account to produce emulsions containing very small droplets.

Energy intensity. The breakup of lipid droplets within a homogenizer depends on the disruptive forces being large enough to overcome the interfacial forces holding the droplets together (McClements 2005a). These interfacial forces increase with decreasing droplet diameter: $\Delta P = 4\gamma/d$, where γ is the interfacial tension and d is the droplet diameter. Hence, it is necessary to generate extremely intense disruptive forces within a homogenizer in order to produce the very small droplets in nanoemulsions. These kinds of intense disruptive forces can be produced using ultrasonic homogenizers or microfluidizers (McClements 2005a; Walstra 1993, 2003; Kentish et al. 2006). The size of the droplets in a nanoemulsion produced by a microfluidizer can usually be decreased by increasing the homogenizer pressure or number of passes.

Viscosity of phases. The efficiency of droplet breakup within a homogenizer also depends on the rheology of the droplets and surrounding medium. Experiments have shown that it is important to ensure that the ratio of dispersed-to-continuous phase viscosity is in a range suitable for facilitating droplet breakup and forming small particles, i.e., $0.5 < \eta_D/\eta_C < 5$ (Wooster et al. 2008, Schubert & Engel 2004, Walstra 1993). The viscosity ratio can be controlled by altering the composition of either the lipid phase (e.g., by mixing low- and high-viscosity oils) or the aqueous phase (e.g., by mixing viscous cosolvents with water). Alternatively, the viscosity ratio can be altered by increasing the homogenization temperature because the viscosity of many oils decreases rapidly with increasing temperature.

Emulsifier properties. The ability to form very small droplets during homogenization is also dependent on the nature and concentration of emulsifier used. An adequate amount of emulsifier must be present during homogenization to coat all of the droplets formed: $c_E = 6\Gamma\phi/d_{32}$, where c_E is the emulsifier concentration per unit volume of emulsion, Γ is the surface load, ϕ is the disperse phase volume fraction, and d_{32} is the surface-weighted droplet diameter. Thus, approximately 10 kg m^{-3} (1%) emulsifier would be required to create a 10 vol% oil-in-water emulsion with a droplet diameter of 60 nm using an emulsifier with a surface load of 1 mg m^{-2}. In practice, the emulsifier concentration actually used may have to be considerably higher than this value because the surface load of many food emulsifiers is above 1 mg m^{-2}, not all of the emulsifier will be present at the oil-water interface, and it takes a finite time for emulsifier to adsorb to the droplet surfaces during homogenization. The tendency for droplet coalescence to occur within a homogenizer depends on the relative time scales of emulsifier adsorption and droplet-droplet collisions. If droplet-droplet collisions occur much faster than the time required to completely coat the droplet surfaces with emulsifier, then droplet coalescence occurs within the homogenizer, thereby increasing the size of the droplets produced. On the other hand, if there is sufficient emulsifier present and it adsorbs fast enough to form a protective coating around the lipid droplets before they have chance to collide with each other, then the droplets produced will remain small. Consequently, one would expect an emulsifier with faster adsorption kinetics to produce smaller droplets. As mentioned above, the ability to produce small droplets within a homogenizer also depends on the magnitude of the disruptive forces generated within the homogenizer compared with the magnitude of the interfacial forces holding the droplets together ($\Delta P = 4\gamma/d$). These interfacial forces decrease as the interfacial tension decreases, so one would expect an emulsifier that is able to decrease the surface tension more effectively would be able to produce smaller droplets.

Potential advantages and limitations. In this section, we summarize the potential advantages and disadvantages of using nanoemulsions within the food industry.

Potential advantages.

- They are fairly easy to prepare compared with more sophisticated structured emulsion-based systems.
- They are useful when optical clarity is required in a product.
- They usually have good stability to gravitational separation, flocculation, and coalescence.
- They are useful when rapid release and/or absorption of functional components is required because of their small size and large surface area.

Potential disadvantages.

- There are only a limited number of food-grade emulsifiers available to stabilize them, which limits the potential for engineering novel or improved functional performance into products.
- A relatively large concentration of emulsifier is required to cover all the droplet surfaces formed during homogenization, which may be costly or produce off-flavors.
- There is limited ability to protect and control the release of functional components because the small size of the droplets (~μm) and the interfacial layers (~nm) means that the timescales for molecular diffusion of substances are extremely short.

Solid Lipid Particles

Solid lipid particle (SLP) emulsions are similar to emulsions and nanoemulsions because they consist of emulsifier-coated lipid droplets dispersed in an aqueous continuous phase (**Figure 3**). However, the lipid phase is either fully or partially solidified, and the morphology and packing of the crystals within the lipid phase are usually controlled (**Figure 5**) to obtain particular functional attributes (Saupe et al. 2005, Souto et al. 2004, Uner et al. 2004, Wissing et al. 2004, Wissing & Muller 2002).

Structure and properties. As with conventional emulsions or nanoemulsions, the size and concentration of the lipid droplets in SLP emulsions can be controlled as well as the nature of the

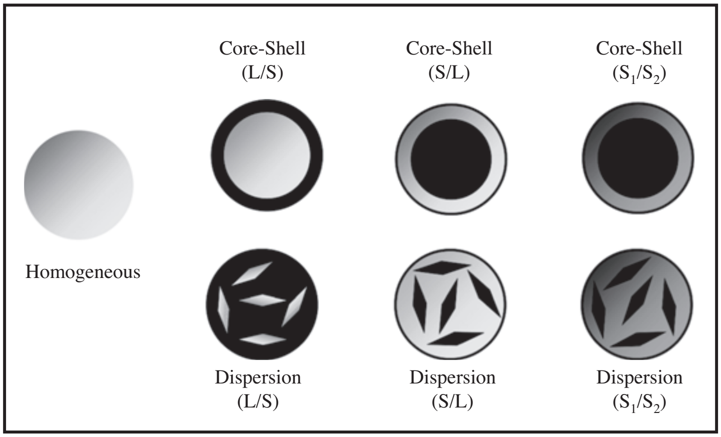

Figure 5

Examples of different kinds of structural organization possible within lipid droplets containing solid fat crystals.

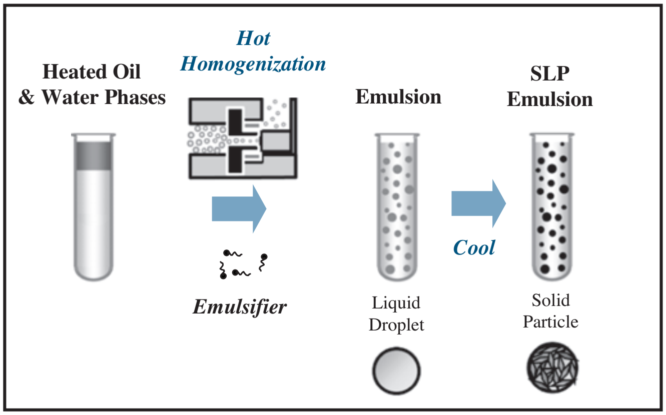

Figure 6

Solid lipid particles (SLPs) are typically produced by homogenizing an oil phase and aqueous phase together in the presence of a water-soluble emulsifier at a temperature above the melting point of the lipid phase. The emulsion is then cooled to promote fat crystallization.

interfacial coating surrounding the lipid phase (e.g., its charge, thickness, permeability, and environmental responsiveness).

Preparation procedures. SLP emulsions are usually created by homogenizing an oil phase and an aqueous phase together in the presence of a water-soluble emulsifier at a temperature above the melting point of the lipid phase (**Figure 6**) (Saupe et al. 2005, Souto et al. 2004, Uner et al. 2004, Wissing et al. 2004, Wissing & Muller 2002, Schubert & Muller-Goymann 2005). The emulsion initially formed at these elevated temperatures contains liquid droplets. The emulsion is then cooled under controlled conditions so that a portion or the entirety of the lipid phase crystallizes. It is crucial that the emulsion is kept above the crystallization temperature of the lipid phase during homogenization, otherwise the homogenizer may be blocked and damaged. The stability of the lipid droplets produced and the spatial organization of the lipid crystals within the droplets are usually controlled by careful selection of the number and type of lipids present, the nature of the surfactant(s) used to stabilize the droplets, the initial droplet size and concentration, and the cooling conditions (Muller & Keck 2004, Muller et al. 2000). In principle, it is possible to create a variety of different internal structures within solid lipid particles, e.g., homogeneous crystal structure, core-shell structures, or crystal dispersions (**Figure 5**). In addition, it is possible to control the relative location of the different phases within the droplets, e.g., the core could be solid and the shell liquid, or vice versa. The structure and spatial organization of the fat crystals within the lipid droplets have important consequences for designing SLP emulsions for encapsulating, protecting, and delivering lipophilic components. For example, in some applications it may be beneficial to locate the lipophilic component within the core (away from any hydrophilic reactive species), whereas in other situations it may be more important to locate it close to the droplet surface (to facilitate its release). Typically, two or more lipids with different melting profiles are used to create specific microstructures within SLP, e.g., mixtures of purified triglycerides, complex triglyceride mixtures, waxes, or fatty acids (Dubes et al. 2003, Saupe et al. 2005, Souto et al. 2004, Uner et al. 2004, Wissing et al. 2004, Wissing & Muller 2002). Utilization of a number of lipids, rather than an individual lipid, usually increases the loading capacity and retention of encapsulated lipophilic components because they can fit better into the more imperfect crystalline structure. The nature of the emulsifier used to stabilize the lipid droplets may also be important in creating specific internal structures. For example, the tail groups of certain surfactants act as templates that promote nucleation within lipids located at the oil-water interface, i.e., heterogeneous surface nucleation (Sonoda et al. 2006). This principle can be used to form core-shell particles with a solid shell and a liquid core. A lipophilic component is usually dissolved or dispersed in the lipid phase at ~10°C above the melting temperature of the highest melting lipid. The hot lipid phase is then homogenized with the hot aqueous phase in the presence of a hydrophilic emulsifier to produce an oil-in-water emulsion, which is then cooled in a controlled manner to promote lipid crystallization.

Potential advantages and limitations. Some potential advantages of SLP emulsions over conventional emulsions for application as delivery systems are listed below (Muller & Keck 2004, Muller et al. 2000, Wissing et al. 2004).

Potential advantages.

- The stability of chemically labile lipophilic components can be improved by trapping them within a structured solid matrix (Muller et al. 2000). The molecular mobility of encapsulated lipids and/or reactive chemical species (such as oxygen) can be altered by controlling the physical state and structure of the lipid matrix. For example, a lipid that normally reacts with hydrophilic components in the aqueous phase could be encapsulated within the lipid core and surrounded by a protective shell of inert lipid.
- Delivery systems can be designed for lipophilic functional components (Souto & Muller 2005, Pople & Singh 2006, Jee et al. 2006, Iscan et al. 2005, Uner et al. 2005). For example, a solid lipid phase could be designed to melt at a particular temperature, thereby releasing an encapsulated functional lipid component.
- Stable emulsion-based systems containing crystalline lipophilic components can be created. In conventional O/W emulsions, a crystalline lipophilic component may promote physical instability as a result of partial coalescence (McClements 2005a), but this may be prevented by trapping a solid functional lipid within a solid carrier lipid matrix.
- The density of the lipid phase can be controlled. The density of a solid fat is higher than water, whereas the density of liquid oil is less than that of water. Consequently, it is possible to develop a lipid particle with the same density as the surrounding aqueous phase by selecting the appropriate solid fat content.

Potential disadvantages.

- A major limitation of SLP emulsions is that they must be prepared at elevated temperatures to avoid crystallization of the lipid phase during homogenization. If crystallization does occur, then the homogenizer will be blocked and potentially damaged. However, the high temperatures used may cause chemical degradation of certain types of heat-sensitive lipophilic components and should therefore be limited as much as possible (Ribeiro et al. 2003).
- The lipid phase usually has to be highly saturated so that it has a sufficiently high melting point to form SLP emulsions, which may have an adverse impact on health.

Multiple Emulsions

Multiple emulsions are structurally more complex versions of emulsions and/or nanoemulsions and can be thought of as emulsified emulsions.

Structure and properties. Water-in-oil-in-water (W/O/W) emulsions consist of small water droplets contained within larger oil droplets that are dispersed within an aqueous continuous phase (Garti 1997a,b; Garti & Benichou 2004; Garti & Bisperink 1998) (**Figure 3**). More accurately, water-in-oil-in-water emulsions should be designated as $W_1/O/W_2$ emulsions, with W_1 representing the inner water phase and W_2 representing the outer water phase (which may have different compositions). There are two different interfacial layers in this type of emulsion: the W_1-O layer surrounding the inner water droplets, and the O-W_2 layer surrounding the oil droplets. Consequently, it is usually necessary to use two different types of emulsifier to stabilize W/O/W emulsions: an oil-soluble emulsifier for the inner water droplets and a water-soluble emulsifier for the oil droplets. In this system, it is possible to control the particle size distribution and concentration of both the inner water droplets and the oil droplets as well as the interfacial properties of the W_1-O and O-W_2 layers surrounding the droplets (e.g., thickness, charge, permeability, and environmental responsiveness).

In many respects, multiple emulsions have bulk physicochemical properties similar to those of conventional emulsions. They tend to be cloudy or opaque because the oil droplets have sizes that are on the order of the wavelength of light. Nevertheless, the appearance of multiple emulsions is affected by the fact that light scattering occurs from both the inner water droplets as well as the oil droplets. As with conventional emulsions, the rheology of multiple emulsions varies from low-viscosity liquids in dilute systems to semisolids in concentrated systems, and their viscosity increases appreciably when the droplets are flocculated or a thickening agent is added to the aqueous phase. Nevertheless, the viscosity of a W/O/W emulsion may be appreciably greater than that of a conventional O/W emulsion at the same overall lipid concentration because the water trapped inside the lipid droplets increases the effective volume fraction of the disperse phase. Multiple emulsions are prone to many of the same instability mechanisms as conventional emulsions. However, there are also additional instability mechanisms associated with the presence of the inner water phase. The oil droplets in W/O/W emulsions are susceptible to creaming, flocculation, coalescence, and Ostwald ripening, just as they are in O/W emulsions. The inner water droplets in W/O/W emulsions are also susceptible to flocculation, coalescence, and Ostwald ripening processes. However, they may also become unstable as a result of the diffusion of water molecules between the inner and outer aqueous phases or owing to the expulsion of whole water droplets from the oil droplets. A variety of different strategies have been developed in an attempt to overcome these problems (Benichou et al. 2004a,b; Garti 1997b; Garti & Bisperink 1998; Garti & Benichou 2004), including identification of appropriate combinations of oil and water-soluble emulsifiers, incorporation of biopolymers into the W_1 phase, solidification of the oil phase, and osmotic balancing of the inner and outer water phases to prevent water diffusion (Benichou et al. 2004b, Garti 1997b, Garti & Benichou 2004, Garti & Bisperink 1998).

There is much more scope for controlling ingredient encapsulation, protection, and release characteristics using multiple emulsions than using conventional emulsions (McClements 2005a). In particular, multiple emulsions are particularly suited for the encapsulation of hydrophilic functional components within the inner water phase. Hydrophilic components (e.g., minerals, vitamins, enzymes, proteins, bioactive peptides, and fibers) could be trapped within the internal water phase, which may have benefits in a number of applications (see below).

Preparation procedures. Multiple emulsions of this kind are normally produced using a two-step procedure (**Figure 7**): (*a*) a W_1/O emulsion is produced by homogenizing water, oil and an oil-soluble emulsifier; (*b*) a $W_1/O/W_2$ emulsion is then produced by homogenizing the W_1/O emulsion with an aqueous solution containing a water-soluble emulsifier (Benichou et al. 2004a, Garti 1997b, Garti & Bisperink 1998). Homogenizers used to produce $W_1/O/W_2$ emulsions are similar to those used to produce conventional O/W emulsions, e.g., high-shear mixers, high-pressure homogenizers, colloid mills, ultrasonic homogenizers, and membrane homogenizers (McClements 2005a). Nevertheless, the homogenization conditions used in the second stage are often less intense than those used in the first stage, so as to avoid disruption or expulsion of the W_1 droplets within the oil phase. The size of the water droplets in the W_1/O emulsion can be controlled by varying emulsifier type, emulsifier concentration, and homogenization conditions (e.g., energy intensity and duration) in the first stage. Similarly, the size of the oil droplets in the final W_1/O/W_2 emulsion can be controlled by varying emulsifier type, emulsifier concentration, and homogenization conditions in the second stage. The concentration of water droplets in the W_1/O emulsion can be controlled by using a different ratio of W_1 to oil phase in the first homogenization step, whereas the concentration of oil droplets in the final W_1/O/W_2 emulsion can be controlled by using a different ratio of W_1/O emulsion to W_2 phase in the second homogenization step. Consequently, one has great scope for creating structured delivery systems with different compositions and microstructures based on multiple emulsions.

Functional food components can potentially be located in a number of different molecular and physical environments within a W_1/O/W_2 emulsion. Hydrophilic components can be incorporated into the inner water phase by dispersing them in the W_1 phase prior to the first homogenization step or in the outer water phase by dispersing them in the W_2 phase either before or after the second homogenization step. Lipophilic components can be incorporated into the oil droplets by dispersing them in the oil phase either before or after the first homogenization step. Surface-active components could be located at either the W_1/O or the O/W_2 interface depending on when they were incorporated during the emulsion preparation procedure.

Potential advantages and limitations. In this section, we summarize the potential advantages and disadvantages of using multiple emulsions within the food industry.

Potential advantages.

- Hydrophilic functional components could be encapsulated inside the inner water droplets and released at a controlled rate or in response to specific environmental stimuli, e.g., changes in pH, ionic strength, temperature, surface active components, or enzyme activity in the mouth, stomach, small intestine, or colon.
- Hydrophilic functional components could be protected from chemical degradation by isolating them from other water-soluble ingredients with which they might normally react.
- The overall fat content of food products that normally exist as O/W emulsions (e.g., dressings, mayonnaise, dips, sauces, deserts) could be reduced by loading the oil phase with water droplets.

Potential disadvantages.

- Multiple emulsions are more difficult and expensive to prepare than conventional emulsions because two homogenization steps and two types of emulsifiers are needed.
- Multiple emulsions are highly susceptible to breakdown during storage or when exposed to environmental stresses commonly used in the food industry, such as mechanical forces, thermal processing, chilling, freezing, and dehydration.

Multilayer Emulsions

Multilayer emulsions are basically emulsions or nanoemulsions that contain lipid droplets with a multiple-layered (rather than single-layered) interfacial coating. This coating usually consists of an emulsifier layer with one or more polyelectrolyte layers surrounding it.

Structure and properties. Multilayer oil-in-water emulsions consist of small oil droplets dispersed in an aqueous medium, with each oil droplet surrounded by a nano-laminated shell that typically consists of an emulsifier layer plus one or more biopolymer layers (**Figure 3**). The particle size distribution and concentration of the core-shell particles in multilayer emulsions can be controlled, as can the characteristics of the interfacial layer coating the droplets, e.g., composition, thickness, charge, permeability, and environmental responsiveness.

In many respects, multilayer emulsions have bulk physicochemical properties (e.g., rheology, optical properties, and stability) similar to those of conventional emulsions with similar particle characteristics (e.g., concentration, size distribution, and net charge). Nevertheless, the possibility of precisely engineering the properties of the nano-laminated shells that coat the droplets provides great scope for improving their stability and functional performance (Aoki et al. 2005; Gu et al. 2005; Guzey & McClements 2006a; Guzey & McClements 2007; Mun et al. 2006; Mun et al. 2007a,b). For example, thick and dense interfacial layers can be designed to increase the effective density of multilayer-coated oil droplets, thereby improving their stability to creaming. However, thick and highly charged interfacial layers can be designed to decrease the attractive and increase the repulsive colloidal interactions between multilayer-coated lipid droplets, thereby improving their stability to flocculation and coalescence (Guzey & McClements 2007, Harnsilawat et al. 2006b). Finally, mechanically strong interfacial coatings can be designed to slow down Ostwald ripening in emulsions (Mun & McClements 2006). In addition, the ability to control the properties of multilayer interfacial coatings enables one to engineer novel functional performance into emulsions, such as protection of encapsulated chemically labile components or controlled release of encapsulated functional compounds.

Preparation procedures. The preparation method for the formation of multilayer emulsions is illustrated schematically in **Figure 8** (McClements 2005b, Guzey & McClements 2006a). Initially, an oil-in-water emulsion is prepared by homogenizing an oil and aqueous phase together in the presence of an ionized hydrophilic emulsifier. The resulting primary emulsion consists of small electrically charged oil droplets dispersed in an aqueous continuous phase. An oppositely charged polyelectrolyte is then added to the system so that it adsorbs around the droplets and produces a secondary emulsion consisting of oil droplets coated by a two-layer emulsifier-polyelectrolyte shell. This procedure can be repeated a number of times to form oil droplets coated by nano-laminated shells consisting of three or more layers. The nano-laminated shells can be deposited around the droplets using either a one-step or two-step mixing procedure depending on the charge-pH characteristics of the polyelectrolytes used:

- One-step mixing: An oil-in-water emulsion containing electrically charged droplets is prepared, and it is then directly mixed with a solution containing oppositely charged polyelectrolyte molecules that adsorb to the droplet surfaces through electrostatic attraction.
- Two-step mixing: An oil-in-water emulsion is prepared containing a polyelectrolyte at a pH where there is not a strong electrostatic attraction between the droplets and the polyelectrolyte molecules (e.g., a pH where they are both either negatively or positively charged). The pH of the solution is then adjusted to change the electrical charge on either the droplets and/or the polyelectrolyte molecules so that the polyelectrolyte adsorbs to the droplet surfaces through electrostatic attraction (e.g., a pH where the droplet and polyelectrolyte have opposite charges).

Studies with emulsions containing protein-coated oil droplets and anionic polysaccharides have shown that two-step mixing often produces more stable multilayer emulsions than one-step mixing because the polysaccharide molecules are more evenly distributed throughout the aqueous phase prior to adsorption (Guzey et al. 2004). A washing step may be required between each electrostatic deposition step to remove any excess nonadsorbed polyelectrolyte remaining in the continuous phase. Otherwise, this free polyelectrolyte might interact with the next oppositely charged polyelectrolyte added to the system, thereby altering its tendency to adsorb to the droplet surfaces. Washing can be carried out by centrifugation or ultrafiltration of the emulsion after the coating procedure has been carried out (Guzey & McClements 2006a). Alternatively, the solution conditions can be optimized so that there is little or no free polyelectrolyte remaining in the aqueous phase after the coating step. In some cases, it is possible to breakdown any flocs formed during the preparation of multilayer emulsions by applying mechanical agitation to the system, such as blending, homogenization, or sonication.

A major advantage of using multilayer emulsions is that the properties of the interfacial layer coating the lipid droplets can be systematically controlled, e.g., its composition, charge, thickness, permeability, rheology, and environmental responsiveness (Decher & Schlenoff 2003, Guzey & McClements 2006a). This can be achieved by careful control of system composition and preparation conditions during the production of the multilayer emulsions, e.g., emulsifier type and concentration, polyelectrolyte type and concentration, pH, ionic strength, order of ingredient addition, and mixing conditions (Guzey & McClements 2006a). The ability to systematically control interfacial properties in a rational manner enables one to design coated lipid droplets with improved stability or novel functional performance (see below).

In multilayer emulsions, functional components could be trapped within the oil droplets or within the nano-laminated coating surrounding them. For example, a hydrophobic functional component could be incorporated into the oil phase prior to homogenization, whereas a charged hydrophilic functional component could be incorporated into one or more of the polyelectrolyte layers surrounding the lipid droplets. The functional components could then be retained within the multilayer emulsion until they are released at the site of action in response to a specific environmental stimulus, such as pH, ionic strength, or temperature. This can be achieved by designing the interfacial layer so that its permeability or integrity changes in a well-defined way in response to the environmental trigger (Gu et al. 2006a, Guzey & McClements 2007, Ogawa et al. 2003a).

Potential advantages and limitations. In this section, we summarize the potential advantages and disadvantages of using multilayer emulsions within the food industry.

Potential advantages.

- Multilayer emulsions can be formed entirely from food-grade ingredients (such as surfactants, proteins, polysaccharides, and phospholipids), using processing operations commonly employed by the food industry (such as homogenization and mixing) (Guzey & McClements 2006a).
- Control of the composition and properties of nano-laminated coatings can be used to increase the physical stability of emulsified oils to environmental stresses, such as pH, salt, thermal processing, chilling, freezing, dehydration, and mechanical agitation (Aoki et al. 2005; Gu et al. 2006; Gu et al. 2005; Guzey et al. 2004; Guzey & McClements 2007; Guzey & McClements 2007; Harnsilawat et al. 2006b; Harnsilawat et al. 2006a; McClements 2005b; Ogawa et al. 2003a,b; Ogawa et al. 2004).
- The chemical stability of emulsified lipids can sometimes be can be improved by minimizing interactions between the encapsulated lipids and chemically reactive aqueous phase components by controlling the interfacial charge and thickness, e.g., the oxidative stability of ω-3 fatty acids can be improved by preventing transition metals from coming into close contact with them (McClements & Decker 2000, Klinkesorn et al. 2005). The same approach could

be used to increase the chemical stability of other lipophilic components by keeping the reactants apart, e.g., β-carotene and lycopene.

- The fact that the thickness and permeability of the interfacial coating surrounding the oil droplets can be controlled means that it is possible to control the release rate of encapsulated functional agents (Decher & Schlenoff 2003). For example, the release rate could be slowed down by increasing the thickness or decreasing the permeability of the nano-laminated shell. The properties of nano-laminated shells can often be made to change in response to specific environmental conditions, such as dilution, pH, ionic strength, temperature, or enzyme activity. For example, nano-laminated coatings may completely detach from oil droplet surfaces when the pH is altered because this causes either the emulsifier or the polyelectrolyte to lose its electrical charge (Gu et al. 2006a; Gu et al. 2005; Guzey et al. 2004; Harnsilawat et al. 2006a; Ogawa et al. 2003a,b). Alternatively, the permeability of nano-laminated coatings is often altered when the pH or ionic strength is changed because this changes the strength of electrostatic interactions, which causes swelling or shrinking of the shell (Decher & Schlenoff 2003).

Potential disadvantages.

- Precise control over system composition and preparation procedures is required in order to avoid droplet aggregation through bridging, depletion, and other effects (McClements 2005b, Aoki et al. 2005, Guzey et al. 2004, Ogawa et al. 2003b). The high susceptibility for droplet aggregation to occur during preparation puts a limit on the maximum amount of oil that can be coated using this approach.
- Additional ingredients (e.g., biopolymers for coatings) and processing steps (e.g., mixing) are required to prepare multilayer emulsions compared with conventional emulsions. Consequently, this type of system is more expensive and difficult to prepare.

As well as polyelectrolytes, other types of electrically charged species, such as solid particles, lipid droplets, or cells, can also be used to coat oil droplets. For example, it has recently been shown that the electrostatic deposition approach could be used to form colloidosomes, which consist of large lipid droplets surrounded by a layer of smaller lipid droplets (Gu et al. 2006b). These systems may be useful for the encapsulation and release of functional lipids. For example, lipophilic functional components could be dispersed within either the inner or outer oil droplets. Hence, it may be possible to keep two chemically reactive oil-soluble components separated from each other, or it may be possible to release oil-soluble components at different rates or in response to different environmental triggers. Finally, it should be noted that other kinds of colloidal particles, such as biological cells, starch granules, solid particles, nanotubes, and macroscopic objects, can be coated using the electrostatic deposition method.

Filled Hydrogel Particles

Filled hydrogel particles are a type of structured delivery system that is created by mixing emulsion droplets with a biopolymer system that is capable of phase separating and forming hydrogel particles.

Structure and properties. A filled hydrogel particle consists of oil droplets trapped within a hydrogel particle that is dispersed within an aqueous medium (**Figure 3**). This type of system can therefore be considered to be an oil-in-water-in-water (O/W_1/W_2) emulsion, where W_1 and W_2 refer to two aqueous phases with different compositions. Typically, the inner water phase (W_1) is a hydrocolloid gel, whereas the outer water phase (W_2) is a liquid that may or may not contain hydrocolloids. The particle size distribution, concentration, physical state, and spatial location of the oil droplets within the hydrogel particles can be varied, as well as the size and properties of the hydrogel particles themselves, e.g., their charge, stability, compatibility, permeability, and environmental responsiveness.

Filled hydrogel particles often have bulk physicochemical properties (e.g., optical properties, rheology, stability, and release characteristics) different from those of conventional emulsions with similar oil droplet concentrations. This kind of system tends to be cloudy or opaque because the oil droplets within the hydrogel particles have sizes that are on the order of the wavelength of light. However, the appearance of filled hydrogel particles is affected by the fact that the droplets are more closely packed and that light scattering also occurs from the hydrogel particles as well as the oil droplets. The viscosity of a suspension of filled hydrogel particles may be appreciably greater than that of a conventional O/W emulsion with the same overall oil concentration because the water trapped inside the hydrogel particles increases the effective volume fraction of the disperse phase. Filled hydrogel particles are prone to many of the same instability mechanisms as conventional emulsions (e.g., gravitational separation, flocculation, coalescence). The oil droplets trapped within hydrogel particles are susceptible to flocculation, coalescence, and Ostwald ripening just as they are in conventional O/W emulsions. In addition, the hydrogel particles themselves are also prone to gravitational separation, flocculation, and coalescence processes. Thus, it is usually necessary to control the colloidal interactions between the hydrogel particles to prevent them from aggregating. The fact that biopolymers have a higher density than water, whereas oil has a lower density, means that it may be possible to match the density of filled hydrogel particles to that of the surrounding water phase and thereby prevent gravitational separation. There is considerably more scope for controlling the release of encapsulated components from filled hydrogel particles than from conventional emulsions. The release rate of emulsified lipophilic compounds can be controlled by changing the composition or dimensions of the hydrogel particles. For example, the release of lipophilic flavors from lipid droplets can be delayed by increasing the dimensions of the hydrogel particles surrounding them because this increases the path that the flavor molecules must diffuse before they are released into the surrounding aqueous phase (Malone & Appelqvist 2003, Malone et al. 2003).

Preparation procedures. Filled hydrogel particles can be prepared using a variety of different approaches (Pich & Adler 2007, Chen et al. 2006, Norton & Frith 2001, Zhang et al. 2007, Burey et al. 2008). Most of these methods initially involve the formation of an oil-in-water emulsion by homogenizing an oil phase together with an aqueous phase containing a water-soluble emulsifier (**Figure 4**). The size, concentration, and charge of the droplets in these emulsions can be controlled by selecting an appropriate emulsifier (type and concentration) and homogenization procedure (homogenizer type and operating conditions). Any lipophilic compounds can be encapsulated within the lipid phase prior to homogenization. A filled hydrogel particle can then be created by combining this O/W emulsion with an appropriate biopolymer solution and then adjusting the solution or environmental conditions to promote hydrogel particle formation (**Figure 9**). A number of approaches that can be used to form filled hydrogel particles are summarized below.

Simple coacervation methods. Under certain conditions, biopolymer molecules dispersed within an aqueous solution can be made to self-associate and form a separate phase by adjusting the quality of the solvent, e.g., by changing dielectric constant, temperature, pH, or ionic strength (Chen et al. 2006, Burey et al. 2008, Malone & Appelqvist 2003). This process is usually referred to as simple coacervation and can be used to form filled hydrogel particles (**Figure 9**). For example, the

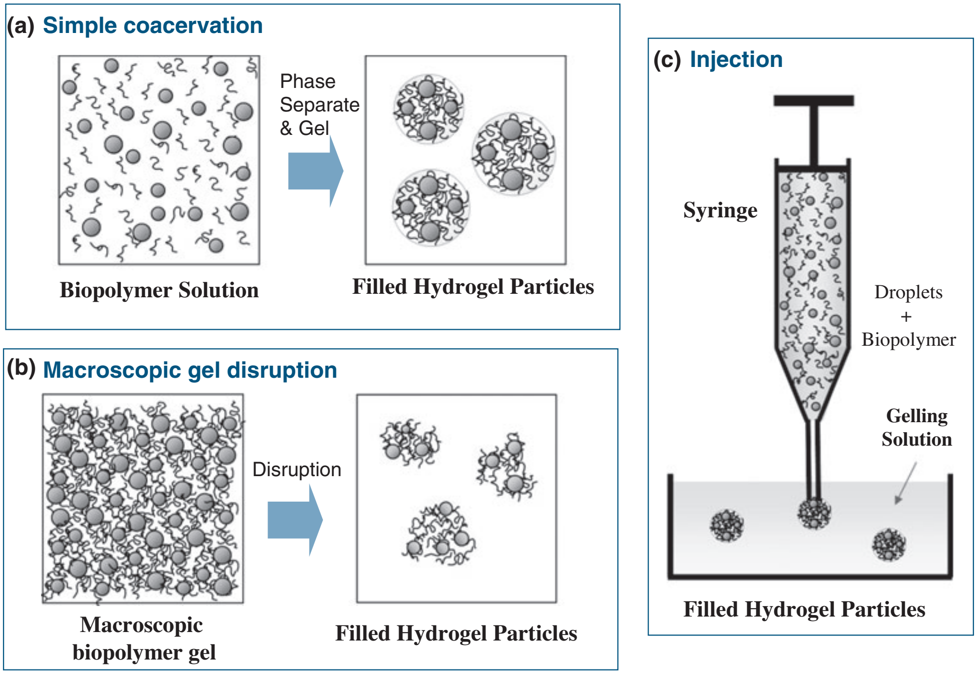

Figure 9

Filled hydrogel particles can be formed using a variety of different procedures. This figure demonstrates how filled hydrogel particles can be formed by (*a*) simple coacervation, (*b*) macroscopic gel disruption, and (*c*) injection methods.

lipid droplets could be mixed with the biopolymer solution prior to adjusting the solvent quality. The solvent quality could then be adjusted to promote the formation of small hydrogel particles that trap the lipid droplets within them (which would require careful selection of lipid droplet surface characteristics and biopolymer type). If necessary, the solution conditions could then be further adjusted to promote gelation of the biopolymer molecules within the hydrogel droplets. In this case, it is important to ensure that the biopolymer concentration is not too high, or else gelation of the whole system may occur.

Macroscopic gel disruption methods. It is also possible to form hydrogel particles by initially forming a macroscopic gel and then applying some kind of mechanical force (e.g., shearing, ultrasonics, microfluidization) to disrupt it (Burey et al. 2008). For example, a macroscopic gel could be formed by changing the environmental or solution conditions of a biopolymer solution, e.g., pH, ionic strength, ion type, temperature, dielectric constant, or enzyme addition. This gel could then be sheared using a high-speed blender to break the gel into smaller particles. The size and shape of the particles formed will depend on the type, intensity, and duration of the mechanical forces applied, as well as the nature of the original macroscopic hydrogel. A similar method could be used to form filled hydrogel particles by applying mechanical disruption to a filled macroscopic gel (**Figure 9**).

Injection methods. Instead of forming the hydrogel particles directly within a solution as described above, it is also possible to form them by injecting a biopolymer solution into another aqueous solution that promotes gelation. In this case, a biopolymer solution is used that is capable of forming a gel when the solution or environmental conditions are altered in a specific manner, e.g., heating, cooling, mineral addition, pH adjustment, or enzyme treatment. Small hydrogel particles are formed by injecting a biopolymer solution that is liquid into an aqueous phase that promotes biopolymer gelation (Senuma et al. 2000, Zhang et al. 2007). For example, a sodium alginate solution could be injected into a calcium solution to form alginate beads. The size of the particles produced can be controlled by varying the injection conditions, e.g., pore sizes, injection volume, injection flow rates, or stirring conditions (Zhang et al. 2007). This process can be adapted to form filled hydrogel particles (Zhang et al. 2006). The lipid droplets are mixed with the biopolymer solution prior to gelation, and the resulting mixture is then injected into another liquid that promotes rapid biopolymer gelation (**Figure 9**).

Emulsion methods. Filled hydrogel particles can also be formed by gelling biopolymer solutions trapped within emulsions. An oil-in-water-in-oil (O/W/O) emulsion is formed by homogenizing an O/W emulsion with an (outer) oil phase containing a lipophilic emulsifier (Cho et al. 2003, Ribeiro et al. 1999). The (inner) oil phase of the O/W emulsion contains the lipophilic component that is to be encapsulated, whereas the water phase contains a biopolymer that is capable of forming a gel under suitable conditions. After the O/W/O emulsion has been produced, the gelation of the biopolymer solution is induced, e.g., enzymatically, chemically, or thermally (Cho et al. 2003, Ribeiro et al. 1999, Hwang et al. 2005). Biopolymer gelation can be achieved by altering the environmental conditions of an O/W/O emulsion, e.g., by heating or cooling. Alternatively, an O/W/O emulsion containing biopolymers within the water phase (e.g., alginate or pectin) can be mixed with a W/O emulsion containing a gelling agent within its water phase (e.g., calcium). When the different types of water-soluble components encounter each other, the biopolymers in the water phase are gelled. Once the aqueous phase containing the biopolymer has gelled, the oil phase is removed from the O/W/O emulsion by centrifuging or filtering to collect the W/O droplets, followed by washing with an organic solvent and drying to remove any excess external oil. Alternatively, the O/W/O emulsion can be formed by homogenizing an O/W emulsion with an organic solvent that acts as the outer oil phase, which can then be removed by evaporation (Freitas et al. 2005). Finally, the filled hydrogel particles are collected and can be used directly or dispersed in water. The size and properties of the internal oil droplets can be controlled by varying the composition (e.g., emulsifier type and concentration) and homogenization conditions (e.g., duration and intensity) used to produce the initial O/W emulsion, whereas the size and properties of the hydrogel particles can be controlled by varying the composition and homogenization conditions used to produce the O/W/O emulsion.

Aggregative separation of mixed biopolymer solutions. If an aqueous solution contains two different kinds of biopolymer molecules that have a sufficiently strong attraction between them, then it will separate into two aqueous phases (**Figure 10**): a phase that is rich in both types of biopolymers, and a phase that is depleted in both types of biopolymers (Burgess 1990, Cooper et al. 2005, de Kruif et al. 2004, Renard et al. 2002, Weinbreck et al. 2003). For food systems, the major driving force for this type of phase separation is usually electrostatic attraction between oppositely charged biopolymers, e.g., an anionic polysaccharide and a cationic protein (Benichou et al. 2002, Desai & Park 2005, Weinbreck et al. 2004, Renken & Hunkeler 1998, Schmitt et al. 1998, Madene et al. 2006). The biopolymer-rich phase may either be a coacervate or a precipitate depending on the strength of the electrostatic attraction and the charge densities of the two biopolymers (Cooper et al. 2005). Coacervates form when the attraction between the two biopolymers is not too strong, and they tend to have more open and dynamic structures. On the other hand, precipitates form when the attraction between the two biopolymers is strong, and they tend to form more densely packed structures. Coacervates are usually better suited for encapsulating oil droplets because they tend to form particles with more well-defined properties (size and charge) and with better stability to aggregation and sedimentation. Small coacervate droplets can be formed when a mixed biopolymer solution is adjusted to conditions where complex coacervation is favored (Cooper et al. 2005). For example, a protein and anionic polysaccharide are mixed together in an aqueous solution at neutral pH, where they are both negatively charged, and then the pH is lowered to a value that promotes electrostatic attraction between positive patches on the protein surface and anionic groups on the polysaccharide. The coacervate droplets formed are often highly susceptible to coalescence and may dissociate when either the pH or ionic strength of the solution is adjusted outside the range favorable to coacervate formation. Consequently, it may be necessary to stabilize the coacervate droplets so that one or both of the biopolymers forms a gel, e.g., by heating, cooling, mineral addition, or enzyme treatment.

Filled hydrogel particles could be created based on this approach by mixing an O/W emulsion with a mixed biopolymer solution before inducing complex coacervation. After coacervation is induced, the coacervate phase forms around the oil droplets and traps them within the coacervate particles (**Figure 11**). Alternatively, the O/W emulsion could be mixed with a preformed coacervate phase and then the filled coacervate phase could be injected into or blended with an aqueous solution. Once formed, the coacervate phase may be cross-linked using the methods described in the previous paragraph.

Segregative separation of mixed biopolymer solutions. If an aqueous solution contains two different kinds of biopolymers (A and B) that have a sufficiently strong repulsive force between them (**Figure 10**), then it may separate into two aqueous phases (Benichou et al. 2002; Norton & Frith 2001; Schmitt et al. 1998; Tolstoguzov 2002, 2003). One of the phases is rich in biopolymer A and depleted in biopolymer B, whereas the other phase is rich in biopolymer B and depleted in biopolymer A. Typically, the driving force for this kind of phase separation is steric exclusion or electrostatic repulsion. When the solution conditions are adjusted so that segregative separation is promoted in a mixed biopolymer solution, the system often initially forms droplets of one phase dispersed in a continuous medium of the other phase. This kind of system can be referred to as a water-in-water (W/W) emulsion. As with coacervates, the water droplets formed as a result of segregative separation are often unstable to coalescence and gravitational separation and so it may be necessary to stabilize them by adjusting the solution or environmental conditions so that one or both of the water phases gels, e.g., by heating, cooling, mineral addition, or enzyme treatment. In this case, filled hydrogel particles could be formed by mixing the O/W emulsion with the mixed biopolymer solution prior to inducing segregative phase separation or by mixing the O/W emulsion with the biopolymer phase that will become the dispersed phase of the W/W emulsion and then incorporating this into the biopolymer phase that will become the continuous phase (e.g., by mixing, injecting, or spraying).

Controlling filled hydrogel particle properties. Filled hydrogel particles with different dimensions, microstructures, and functional properties can be created by varying the nature of the biopolymers involved (e.g., charge, molecular weight, flexibility, hydrophobicity), the solution composition (e.g., pH, ionic strength, dielectric constant), the mixing conditions (e.g., order of addition, stirring speed, homogenization pressure), and the environmental conditions (e.g., temperature or pressure). Thus, it is possible to prepare hydrogel particles that have different compositions, sizes, shapes, electrical charges, porosity, loading capacities, release properties, and environmental responsiveness. Functional lipophilic components can be encapsulated within the oil phase prior to formation of the initial O/W emulsion. In addition, hydrophilic functional components can be encapsulated within the hydrogel particles or the surrounding aqueous phase, e.g., peptides, minerals, chelating agents. This kind of system is already used in the pharmaceutical industry for drug delivery and is likely to gain increasing utilization within the food industry once suitable food-grade formulations and preparation conditions have been identified.

Potential advantages and limitations. In this section, we summarize the potential advantages and disadvantages of using filled hydrogel particles within the food industry.

Potential advantages

- Filled hydrogel particles can be formed entirely from food-grade ingredients (such as proteins, polysaccharides, and lipids), using processing operations already commonly used by the food industry (such as mixing, temperature control, and pH adjustment).
- The composition and properties of hydrogel particles can be designed to protect encapsulated lipids against chemical degradation, such as ω-3 fatty acids (Lamprecht et al. 2001, Wu et al. 2005) and flavor oils (Weinbreck et al. 2004).
- The composition, dimensions, permeability, and environmental responsiveness of the hydrogel particles could be designed to control the release of encapsulated components, e.g., flavors or nutraceuticals (Malone & Appelqvist 2003, Malone et al. 2003). The release rate of an encapsulated component could be controlled by increasing the size or by decreasing the permeability of the hydrogel particle. The hydrogel particle could also be designed so that it released the functional components at the appropriate site within the human digestive system, e.g., the mouth, stomach, or small intestine. This could be achieved by altering the swelling/shrinking of the hydrogel particle or promoting its degradation/dissolution under different temperature, pH, salt, or enzyme conditions.

Potential disadvantages.

- Filled hydrogel particles are more difficult to prepare than conventional emulsions, requiring additional ingredients (e.g., proteins, polysaccharides, and cross-linkers) and additional processing operations (such as careful mixing, pH control, and cross-linking conditions). Consequently, their production is likely to be more expensive and more prone to failure.

INTEGRATED STRUCTURED-EMULSION SYSTEMS

In the previous sections, a variety of delivery systems based on structured emulsion technology was highlighted. It is possible to form other types of structures by combining two or more of these methods. The multilayer approach could be used to form nano-laminated coatings around the particles in nanoemulsions, solid lipid particles, multiple emulsions, liposome suspensions, or filled hydrogel particles. Hydrogel particles could be loaded with nanoemulsion droplets, multilayer coated droplets, solid lipid particles or multiple emulsion droplets. There is, therefore, considerable potential for the formation of novel structured emulsions based on utilization of a few basic principles.

CONCLUSIONS

A wide variety of structured emulsion systems are currently available for the encapsulation of functional food lipids, each with its own advantages and disadvantages. This review has provided an overview of the major types of structured emulsion systems currently available, including a discussion of their preparation, and their potential advantages and disadvantages for application in foods. Conventional oil-in-water emulsions are currently the most widely used system in the food industry at present, but they are often susceptible to breakdown over time or when they are exposed to certain environmental stresses during production, transport, storage, or utilization. In addition, they only have limited capacity to encapsulate, protect, and deliver certain types of functional components. Consequently, for certain applications there is a need to develop more sophisticated delivery systems with improved or novel functional performance. Other types of lipid-based delivery systems, such as nanoemulsions, solid lipid particles, multiple emulsions, multilayer emulsions, and filled hydrogel particles, have certain advantages over conventional emulsions, but they are often expensive and difficult to prepare and are sometimes more unstable. Consequently, their application should only be considered where cheaper and simpler alternatives will not provide the desired functionality.

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The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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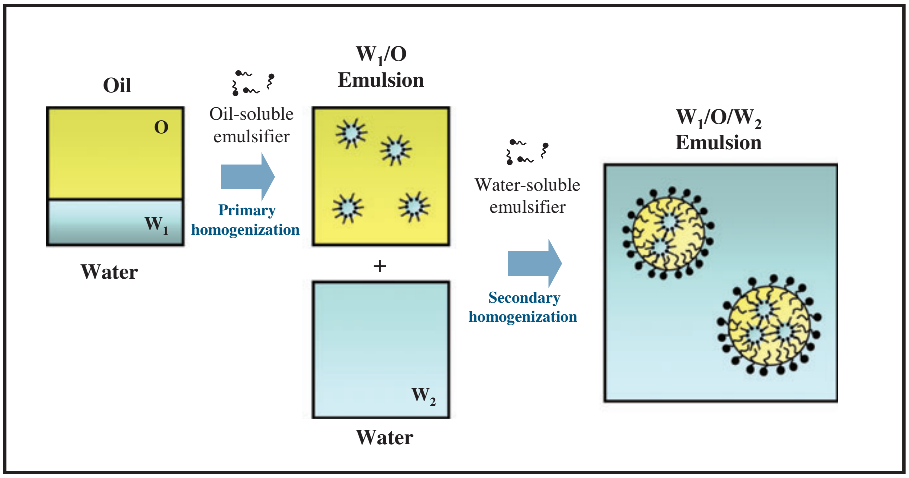

Figure 7

Multiple emulsions (W/O/W) are usually produced using a two-step procedure. (*a*) Primary homogenization: oil and aqueous phases are homogenized together in the presence of an oil-soluble emulsifier to form a W/O emulsion. (*b*) Secondary homogenization: the W/O emulsion is homogenized with a water phase in the presence of a water-soluble emulsifier to form a W/O/W emulsion.

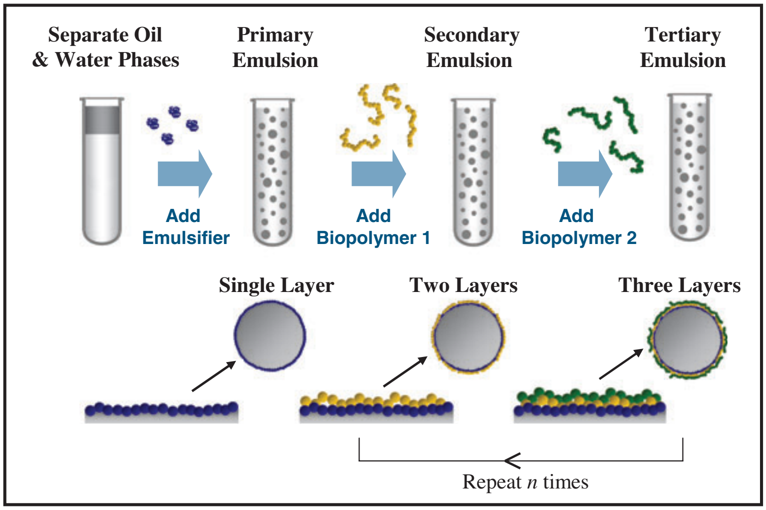

Figure 8

Multilayer emulsions are produced by a multistep procedure: (*a*) Primary emulsion: an oil and aqueous phase are homogenized together in the presence of a charged water-soluble emulsifier. (*b*) Secondary emulsion: an oppositely charged polyelectrolyte is added to coat the droplets. (*c*) Multilayer emulsions: sequential polyelectrolyte adsorption steps can be carried out.

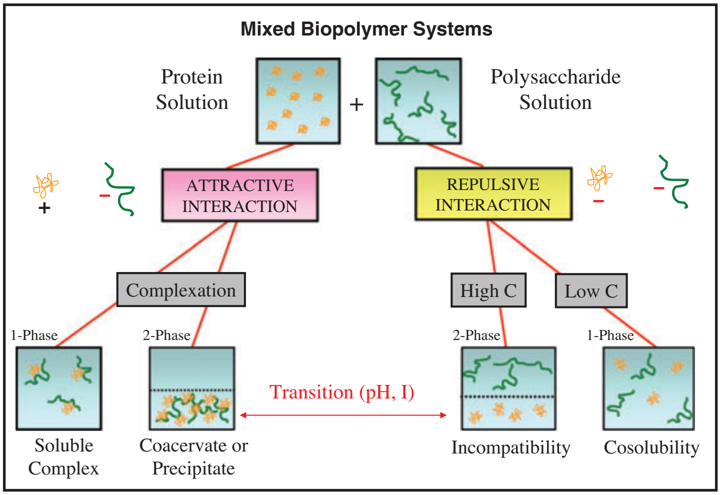

Figure 10

Mixed biopolymer solutions may phase separately under conditions where there are either attractive or repulsive interactions between the biopolymer molecules.

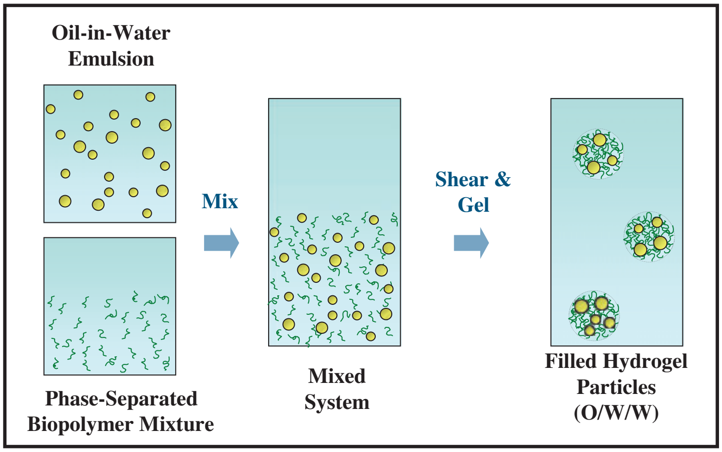

Figure 11

Filled hydrogel particles can be formed from phase-separated biopolymer solutions. In the example shown, an O/W emulsion is mixed with a phase-separated biopolymer mixture in which the oil droplets partition into the biopolymer phase that later forms the hydrogel particles. The resultant mixture is stirred to create biopolymer particles containing lipid droplets, and then the conditions are altered to gel the inner biopolymer phase and form filled hydrogel particles.

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Contents

Errata

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