

Chapter 5

Emulsifying Properties



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Abstract To date, food hydrocolloids have been extensively studied as a surface-active ingredient adsorbing at the oil–water interface to stabilize emulsions through the interfacial properties. This chapter is aimed to review the formation, preparation methods, colloidal properties, and stability mechanisms of food emulsions. The effects of the absorbing and non-absorbing food hydrocolloids on the flocculation, coalescence, creaming/sedimentation, and Ostwald ripening of emulsions are discussed. Three classes of food hydrocolloids as emulsifiers are categorized: proteins (e.g., gelatin, zein, whey protein, casein, and β -lactoglobulin), polysaccharides (e.g., gum arabic, pectin, galactomannan, microcrystalline cellulose, and starch), and protein-polysaccharide conjugates, which can be covalently or electrostatically formed to provide the improved emulsifying and stabilizing properties. Due to the unique emulsifying properties, these food hydrocolloids have found a number of applications in beverages, dairy and meat products in the food industry. The future prospects of food hydrocolloids with emulsifying properties are proposed at the end of this chapter.

Keywords Emulsion stability · Emulsifier · Protein · Polysaccharide · Conjugates

1 Introduction

An emulsion is a colloid of two or more immiscible liquids where one liquid acts as a continuous phase and other liquids discontinuously disperse in it. During emulsion preparation, an emulsifying agent actively adsorbs at the newly formed oil–water interface to protect the newly formed droplets from immediate coalescence. Except

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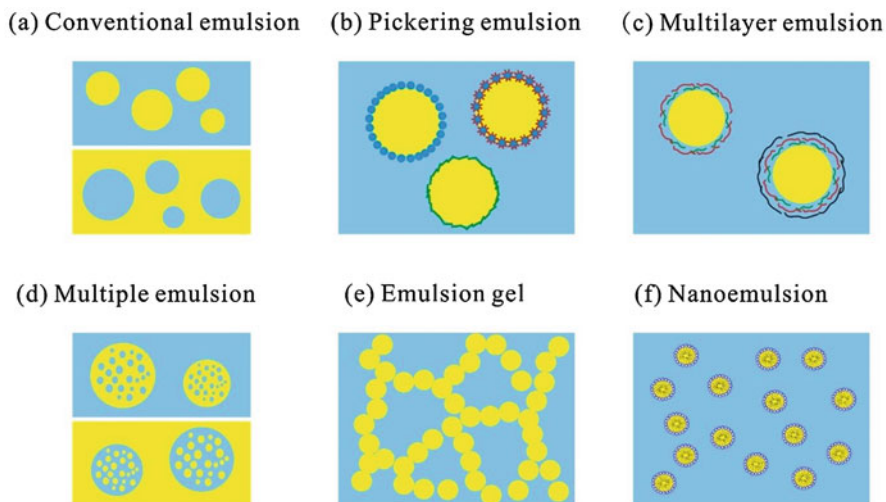


Fig. 5.1 Structures of conventional emulsion (a), Pickering emulsion (b), multilayer emulsion (c), multiple emulsion (d), emulsion gel (e), and nanoemulsion (f)

for small molecular surfactants, food hydrocolloids are traditionally associated with thickening and gelling behaviors, which result in enhanced emulsion viscosity and retard the movement of oil droplets. On the other hand, there are some hydrocolloids which can influence the emulsion stability through the interfacial properties. Hence, a food hydrocolloid may serve as an emulsifier, as a stabilizer, or in both of these roles.

Based on the dispersed and continuous phase, food emulsions are commonly divided into two conventional emulsions, which are water-in-oil (W/O) and oil-in-water (W/O) emulsions. Additionally, the preparation of several sophisticated emulsions has been of wide interest to the food scientists (Fig. 5.1). Examples are Pickering emulsions, multilayer emulsions, multiple emulsions, emulsion gels, nanoemulsions, etc. (Sivapratha and Sarkar 2018). Nanoemulsions are dispersions of nanoscale droplets with a mean droplet diameter between 20 and 100 nm (Solans et al. 2005). The mean droplet diameter of nanoemulsions sometimes is the same as microemulsions, but the two systems are quite different, as nanoemulsions are thermodynamically unstable while microemulsions are thermodynamically stable (McClements 2012). In Pickering emulsions, solid particles are partly wetted by oil and water, and act as a physical stabilizer based on a steric mechanism (Chevalier and Bolzinger 2013). A densely packed layer composed of particles at the oil–water interface contributes to the formation of Pickering emulsions. Multilayer emulsions are usually fabricated by layer-by-layer electrostatic attraction. Water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) emulsions are referred to as “emulsions of emulsions,” where the droplets of one dispersed liquid are further dispersed in another liquid (Benichou et al. 2007). Emulsions containing hydrogels have recently emerged as a new class of functional materials, which offer the advantage of

improved mechanical resistance for easier handling, and the opportunity for hydrophilic bioactive delivery (Dickinson 2012) as well as healthier fat replacers (Freire et al. 2018).

2 Methods for Creating Emulsion Systems

The homogenization process usually contains a single step or some consecutive steps, which is of great necessity to create an emulsion system from two immiscible liquids. During homogenization, a variety of methods for preparing emulsions greatly affect the flow conditions (i.e., laminar, turbulent, or cavitational) of emulsions, which determine the nature of the forces for disrupting a droplet. The methods such as high-speed mixers, colloid mills, high-pressure valve homogenization, ultrasonication, microfluidization, and membrane and microchannel homogenization are high-energy ones, while phase inversion and spontaneous emulsification techniques belong to low-energy methods (Fig. 5.2). Comparatively, low-energy methods are more applicable in the preparation of nanoemulsions, in which fine oil droplets are inclined to the spontaneous formation under specific environmental conditions (e.g., composition, stirring, temperature) (Rao and McClements 2010). Owing to less equipment requirement and energy costs, low-energy methods are attractive in the food and beverage industries. However, in low-energy methods, only a few types of oils and emulsifiers are suitable for preparing stable ultrafine droplets, and relatively high emulsifier-to-oil ratios are required. High-energy

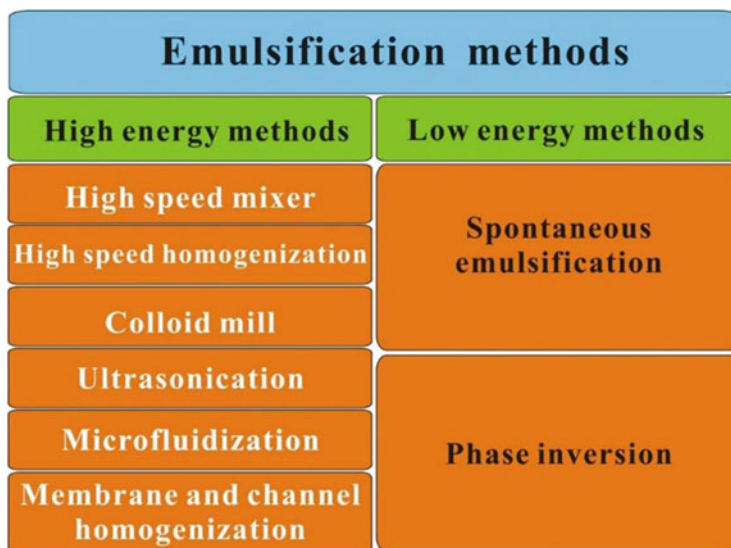


Fig. 5.2 Illustration of the commonly used emulsification methods

methods are often effective for creating other emulsion systems. High-speed mixers and colloid mills are only available to form coarse emulsions, in which emulsion droplets have relatively large droplet sizes ($r > 1\mu\text{m}$), but the other methods can be employed to form submicron droplets. In addition, different types of homogenizers are recommended according to the rheological characteristics of the materials. For example, the homogenization of highly viscous fluids needs the use of some high-speed mixers and colloid mills, while low or intermediate viscous materials can be handled by most other types of homogenizers. Moreover, the different size distribution of droplets can be accomplished by different methods. For the preparation of emulsions with narrow droplet size distributions, membrane and microchannel homogenizers are more effective than other methods. Consequently, a variety of factors (e.g., the rheological characteristics of materials, the desired droplet size distribution) should be considered for selecting an appropriate emulsification method, with a purpose of a particular application (Zhang et al. 2018).

3 Colloidal Properties

The appearance, texture, and shelf life of emulsion products are associated with the droplet size in emulsion systems. In general, the size of the droplets in a monodisperse emulsion is expressed as the droplet diameter or radius, while a particle size distribution is used to denote the fraction of droplets within a range of discrete size classes in a polydisperse emulsion. For low-energy methods, the dominant factors affecting the size distribution of droplets are emulsifier type, emulsifier-oil-water ratio, ionic strength, etc. The size distribution generated by high-energy methods mainly depends on emulsifier type and concentration, oil-water interfacial tension, viscosities of oil and water phases, and the intensity and duration of energy input (Jafari and McClements 2018). A static light scattering instrument is mainly used as a particle size analyzer on condition that the emulsion droplets can scatter incident light in a well-defined manner. But for concentrated emulsions, the extensive dilution and ultrasonic treatment are of necessity before the light scattering measurements to avoid inaccuracy of results. Alternatively, a light microscope is available to achieve the assessment of the microstructure and droplet size distribution of concentrated emulsions.

The interface of each emulsion droplet is a narrow region formed by accumulation of surface-active substances. The type and concentration of surface-active species determine the composition and structure of the interfacial region, which may influence the intermolecular distance and local concentration of reactive molecules, and then accelerate certain types of chemical reactions (e.g., oxidation) (McClements and Decker 2000). Typically, for monolayer emulsions stabilized by food-grade emulsifiers (e.g. proteins, polysaccharides, surfactants), the thickness of the interfacial layer is in the range of 1–10 nm, which is considered as a vital factor for emulsion stability.

Table 5.1 The major colloidal interactions between oil droplets in emulsions (Piorkowski and McClements 2014)

Interactions	Sign	Magnitude	Range
Electrostatic	Repulsive	Strong to weak	Long to short
Steric	Repulsive	Strong	Short
Depletion	Attractive	Weak to medium	Short
Bridging	Attractive	Strong	Short
Van der Waals	Attractive	Intermediate	Intermediate
Hydrophobic	Attractive	Strong	Long

The electric properties of emulsion droplets, usually characterized in terms of zeta-potential (ζ), mainly depend on the solution conditions and the adsorbed emulsifier molecules that are ionized or ionizable (McClements 2010). For example, ionic surfactants in emulsion systems can be neutral, positively charged, or negatively charged. The electrical charge of proteins is associated with the isoelectric point and solution pH. Depending on the type of functional groups along the backbone, surface-active polysaccharides may also have an electrical charge. In general, the emulsion droplets are covered by the same type of emulsifier. Then, the electrostatic repulsion caused by the same electrical charge protects the droplets from aggregation, and significantly affects the interactions between emulsion droplets and other charged species (e.g., surfactants, hydrocolloids, flavors, antioxidants). For instance, the catalyst electrostatically absorbed on the droplet surface may promote the lipid oxidation of oil droplets, in comparison to free one (Mei et al. 1998).

In addition to electrostatic interactions, colloidal interactions such as van der Waals, steric, hydrophobic interactions, depletion, and salt-induced attraction can also play a significant role in emulsion systems (Table 5.1). Their magnitude (strong to weak), sign (attractive to repulsive), and range (long to short) determine the nature of interdroplet interactions, which strongly affect the overall characteristics (e.g., stability, rheology, and appearance) of a particular emulsion system. When attractive forces dominate the interactions, the droplets are inclined to associate with each other. While the dominant forces are repulsive, the droplets tend to retain their individual integrity (Zhang et al. 2018).

4 Emulsion Stability

When considering the stability of an emulsion, the distinguishment between its thermodynamic and kinetic stability is significant. From a thermodynamic point of view, an emulsion tends to separate due to the reduced interfacial energy. Therefore, all food emulsions are thermodynamic instability and will eventually break down as long as they are left long enough (McClements 2015).

The comparison of the free energy of a liquid–liquid system before and after homogenization can be used to explain the origin of such thermodynamically unstable systems. The free energies of an oil phase and a water phase keep constant before and after emulsification, so the difference in the free energy between the non-emulsified and emulsified states is analyzed as follow:

$$\Delta G_{\text{formation}} = G^f - G^i = G_I^f - G_I^i - \left(TS_{\text{config}}^f - TS_{\text{config}}^i \right) = \Delta G_I - T\Delta S_{\text{config}}$$

By definition, the difference in interfacial free energy (ΔG_I) between the initial and final states is equal to the increase in contact area (ΔA) between the oil and water phases, which is multiplied by the interfacial tension (γ): $\Delta G_I = \gamma\Delta A$. Hence,

$$\Delta G_{\text{formation}} = \gamma\Delta A - T\Delta S_{\text{config}}$$

The increased contact area after emulsification always results in the positive change in interfacial free energy, which thus opposes emulsion formation. Additionally, due to the greater number of arrangements accessible to the droplets in the initial state than the final state, the configurational entropy term ($-T\Delta S_{\text{config}}$) is always negative, which therefore contributes to emulsion formation. The overall free energy change concerned with the formation of a food emulsion can thus be expressed by

$$\Delta G_{\text{formation}} = \gamma\Delta A$$

Therefore, the creation of a food emulsion should be always thermodynamically unfavorable, because of the increased interfacial area after emulsification.

Compared with the thermodynamic stability, the kinetic stability of food emulsions is more attractive and interesting for food scientists and engineers, because of the particular importance to create food products with desirable properties. Between the two different free energy states (G_{low} and G_{high}) probably occupied by plenty of molecules in a system, the molecules are most likely to occupy the state with the lowest free energy. At thermodynamic equilibrium, the two states are populated according to the Boltzmann distribution:

$$\frac{n_{\text{high}}}{n_{\text{low}}} = \exp\left(-\frac{(G_{\text{high}} - G_{\text{low}})}{kT}\right)$$

where n_{low} and n_{high} are the number of molecules that occupy the energy levels G_{low} and G_{high} , k is Boltzmann's constant ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$), and T is the absolute temperature.

Compared with the thermal energy of the system (kT), the fraction of molecules in the lower free energy state becomes greater as the difference between the two free energy levels is larger. In practice, due to the presence of a free energy barrier, ΔG^* , between the two states (Fig. 5.3), a free energy needs to be acquired to cross the

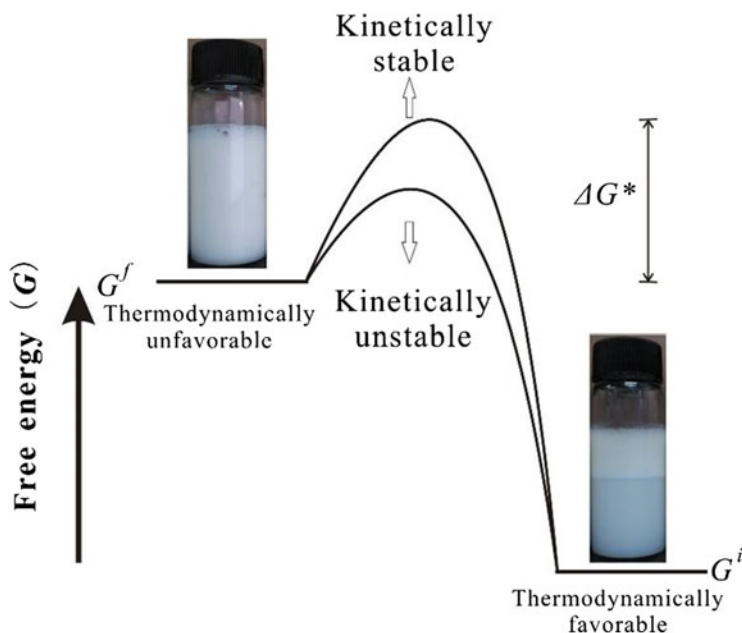


Fig. 5.3 Emulsions are a thermodynamically unstable system, but may exist in a metastable state, therefore being kinetically stable

barrier if a high free energy state of a system moves into a low one, and the transformation rate decreases with the increasing barrier height. In general, the long-term stability of most emulsions needs an activation energy of about $20kT$. Actually, an emulsion system is in different metastable states, probably because of the sufficiently large barrier associated with a thermodynamically unstable state for a long time. Nevertheless, a single free energy barrier concerned with a particular physicochemical process is considered as a most important factor to determine the overall kinetic stability of an emulsion.

5 Stability Mechanisms

The most important phenomena affecting the long-term stability of an emulsion are gravitational separation, coalescence, flocculation, phase inversion, and Ostwald ripening (Fig. 5.4). Creaming, as one type of gravitational separation, describes that droplets in a system move upward owing to their lower density than the surrounding liquid, while sedimentation is the other type of gravitational separation, which describes that droplets move downward because of their higher density than the surrounding liquid. Flocculation and coalescence are both types of droplet aggregation. Flocculation describes the process that two or more droplets come

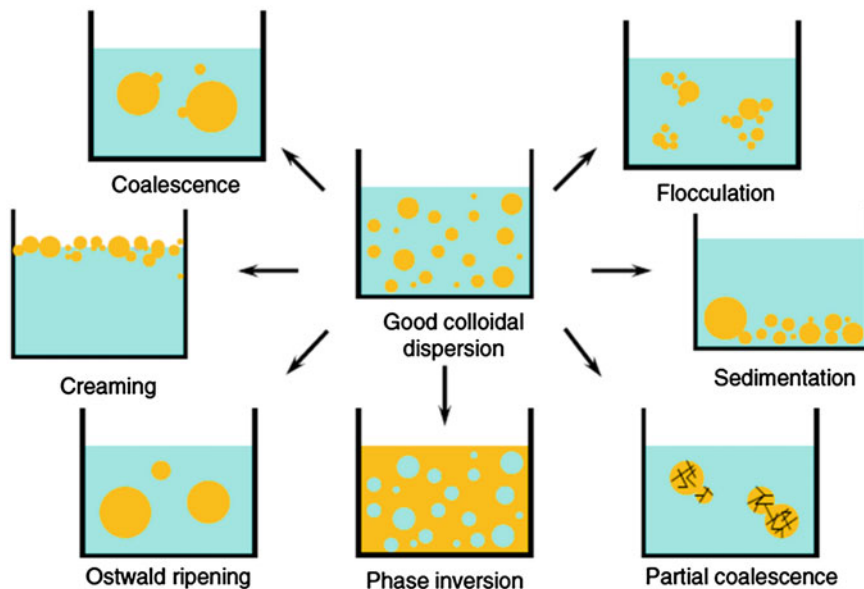


Fig. 5.4 Mechanism of destabilization in a colloidal system. Reproduction with permission from (Kuroiwa et al. 2015), Copyright 2015 Elsevier

together but remain as individual entities, while coalescence occurs when two or more droplets merge together, resulting in the formation of a single larger droplet and eventually a separate layer of oil on the top of a system, namely, “oiling-off.” Phase inversion describes the conversion from an O/W emulsion to a W/O emulsion or vice versa. Ostwald ripening is the growth of one emulsion droplet at the expense of a smaller one as a result of the difference in chemical potential of the material within droplets. Small-sized unstable particles are being dissolved and re-attached on the surface of big particles, reaching a more stable thermodynamic state.

5.1 Flocculation

Flocculation is a reversible process of the sticking together of droplets upon collision, leading to an apparent increase in the droplet size and then an acceleration of creaming or sedimentation. As droplet collisions reduce or electrostatic and steric repulsion increase, flocculation can be decreased between droplets. Once droplets collide, the interface separating two droplets has a naturally thinner tendency and eventually ruptures. Then, coalescence occurs in a form of one larger droplet. Emulsions stabilized with ionic hydrocolloids are more likely sensitive to pH and ionic strength, which would induce flocculation by pH changes or specific types of ions. The conformation of the hydrocolloids is also affected by pH and ionic

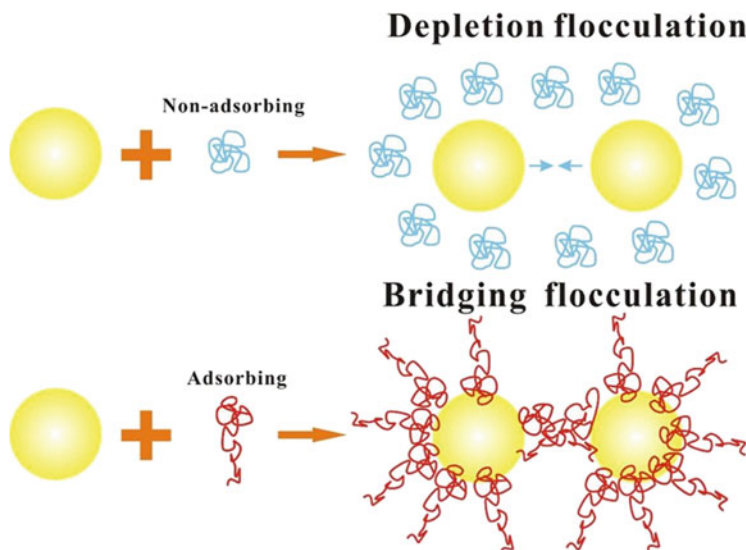


Fig. 5.5 Schematic illustration of depletion and bridging flocculation

strength, especially the protein part. The addition of simple salts into the aqueous phase reduces the thickness of the electrical double-layer, and so diminishes the range of the electrostatic repulsion.

When a polymer is introduced into a colloidal system, flocculation is often observed, due to one of two distinct mechanisms—bridging or depletion flocculation (Fig. 5.5). Bridging flocculation is a process that the insufficient emulsifier cannot achieve the saturation of freshly formed surfaces and share the adsorbed layer among neighboring droplets. When the emulsifier adsorbs too slowly or is present at a very low concentration, most of the individual droplets tend to form an aggregate and cannot remain as their individual integrity as a result of coalescence or bridging flocculation.

If the amount of non-adsorbing hydrocolloids in an emulsion is not enough to immediately cover all the interface, depletion flocculation may occur. McClements (2000) defined four regions concerned with the instability of an emulsion system containing polysaccharides, and determined a critical flocculation concentration (CFC), which is the polysaccharide concentration producing depletion flocculation. When the polysaccharide concentration (c) in an emulsion exceeds a particular value, termed as the critical viscosity concentration (CVC), creaming would be assumed to completely retard: (I) Unstable. No-flocculation ($c < \text{CFC}$) and relatively low viscosity ($c < \text{CVC}$). The droplets move upward at a rate that is proportional to the square of their diameter and the reciprocal of the aqueous phase viscosity. (II) Highly unstable. Flocculation ($c > \text{CFC}$) and relatively low viscosity ($c < \text{CVC}$). The effective size of the particles in the emulsion increases because of flocculation, but the viscosity is not high enough to prevent the flocculation. (III) Stable. No-flocculation ($c < \text{CFC}$) and high viscosity ($c > \text{CVC}$). The droplets are

not flocculated, but the viscosity of the aqueous phase is so large that they cannot move. (IV) Stable. Flocculation ($c > CFC$) and high viscosity ($c > CVC$). The droplets are flocculated, but the viscosity of the aqueous phase is so large that they cannot move.

5.2 Coalescence

Coalescence describes the merging of two or more emulsion droplets to form a larger single droplet. For an emulsion product, coalescence is perceived as highly unfavorable during storage. The shifting of the overall distribution towards larger droplet sizes may result in the enhanced creaming. However, partial coalescence for the development of structures is of great significance for some food products, such as whipped cream and ice cream, because of the conversion of a viscous liquid to a viscoelastic solid. For many of food triglyceride emulsions, particularly dairy emulsions, fat crystallization occurs in such emulsion droplets at storage temperature. Crystals are both radial and tangential to the surface, and actually growing or protruding through the membrane. The incomplete coalescence caused by crystals present in the oil phase results in the formation of irregularly aggregated droplets with the original identity (Fig. 5.6). Two important additional factors influencing partial coalescence are: (i) the temperature cycling of cream layers, which causes growth and melting of fat crystals, and (ii) agitation or stirring, which greatly increases the likelihood of collision-induced crystal penetration between droplets (Dickinson 2009).

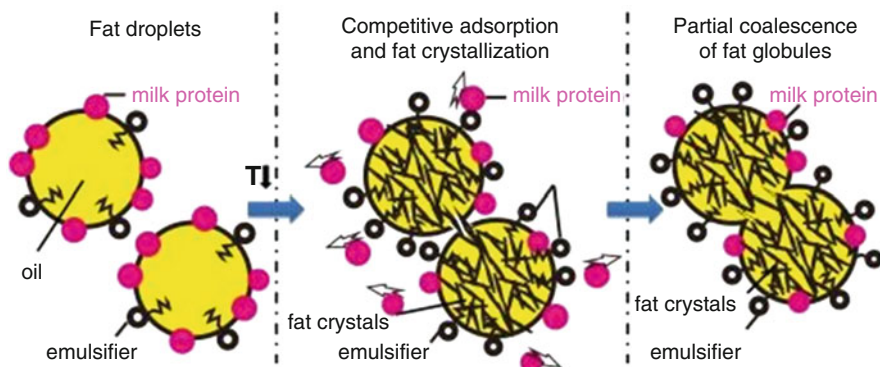


Fig. 5.6 Schematic illustration of fat crystallization and partial coalescence. Reproduction with permission from Cheng et al. (2020) Copyright 2020 Elsevier

5.3 *Creaming/Sedimentation*

Creaming is a process that oil droplets driven by gravity move upward to form a concentrated cream layer at the top of an emulsion. The decreased droplet size of colloidal particles can retard creaming, which can be modified by the hydrocolloid concentration, emulsifying conditions (pH, ionic strength), and emulsification method. Beverage emulsions are sensitive to creaming due to the fact that the dilute emulsions are typically made up of a flavor oil blend containing a weighting agent, and a polymeric emulsifier or stabilizer (Given Jr 2009). Sedimentation also happens when the weighting agent is overused or supersaturated in the oil phase. Various hydrocolloids have been applied for manufacture of beverage flavor emulsions, such as octenyl succinylation starch, whey protein, arabinogalactan, etc. (Klein et al. 2010; Mora-Gutierrez et al. 2018). Electrostatic interactions between proteins and polysaccharides are used to fabricate sequential multilayers to build droplet shell integrity and stability against various environmental stresses (ionic strength, pH, presence of oxidation catalysts, heat, sunlight, etc.), because of the formation of a more robust interfacial complexes.

5.4 *Ostward Ripening*

The difference in the radius of droplet curvature results in the chemical potential of the materials within droplets and then Ostwald ripening, i.e., one emulsion droplet grows at the expense of a smaller one. Alternatively, the process may be purely viewed from a perspective of the reduced free energy in the system by means of the destructed interfacial area. Overall, the effect is an increase in the average radius of the emulsion droplets with time, as the smaller droplets dissolve and redeposit their materials onto the larger droplets (Taylor 1998). In theory, Ostward ripening can be decreased as the monodispersity of an emulsion increases, due to the fact that the thermodynamic driving force is associated with the size difference of droplets. In practice, the coarsening tendency can be reduced by mixing of another insoluble component into the dispersed phase, due to a large counteracting thermodynamic driving force provided in direct opposition to the Ostwald ripening effect (Kabal'Nov et al. 1987; Davis et al. 1981).

6 Proteins

6.1 *Gelatin*

Gelatin is a natural protein hydrolyzed from animal collagen. It is widely used for foaming, emulsifying, and wetting purposes in food industry. Previous studies have

shown that gelatin acts as an emulsifier with surface activity in O/W emulsions (Table 5.2) (Lobo 2002). Its emulsification and foamability derive from the hydrophobic area of peptide chains on gelatin. Compared with other surface-active substances, such as globular proteins and gum arabic, gelatin is a weaker emulsifier, which often produces larger droplet sizes during homogenization when used alone. Hence, its effectiveness can be improved by either hydrophobically modification with the attachment of non-polar side-groups or used in combination with other emulsifiers as complex emulsifiers.

Gelatin from marine sources (warm- and cold-water fish skins, bones, and fins) is a possible alternative to bovine gelatin, with an advantage of being not associated with the risk of bovine spongiform encephalopathy. Moreover, fish gelatin is acceptable in Islam and can be used with minimal restrictions in Judaism and Hinduism. Surh et al. (2006) studied the emulsifying property of fish gelatin with various molecular weights, and the effects of pH, salt, and thermal processing on the stability of the gelatin-stabilized emulsions. It was observed that a higher ratio of large droplets led to an easier destabilization of the emulsions stabilized by low molecular weight fish gelatin than high molecular weight ones. Dickinson and Lopez (2001) compared the emulsifying property of fish gelatin with that of commercial milk proteins, and found that an optimization of the protein/oil ratio was expected to prevent coalescence caused by large droplets, especially at high ionic strength.

Due to the limited emulsifying property of gelatin, its complexes with other emulsifiers have been studied. In a reported study (Surh et al. 2005), the multilayer emulsions with SDS as the first layer and SDS-fish gelatin complex as the second layer were fabricated, the droplets in the secondary emulsions exhibited good stability against droplet aggregation in a water bath for 30 min at different temperatures ranging from 30 to 90 °C. It was also observed that the emulsions prepared with a complex of whey protein with fish gelatin using layer-by-layer interfacial deposition technique were more physiochemically stable than those with individual proteins (Taherian et al. 2011). Zeeb et al. (2011) studied the stabilizing effect of enzymatic crosslinking on the beet pectin-fish gelatin double coated emulsions, and found that the freeze-thaw stability and creaming behavior of the secondary emulsions treated by laccase were significantly improved, compared to the individual emulsions. Lately, the fish gelatin-gum arabic complexes were used to fabricate concentrated emulsions, and greater intermolecular connectivity between the adsorbed layers of adjacent oil droplets for a gel network extension was observed at lower pH (Anvari and Joyner 2017).

6.2 Zein

Zein, as a food-grade abundant material extracted from corn, has been attempted to accomplish extensive applications in various industries. The hydrophobic property of zein depends on its high proportion of hydrophobic amino acids, while the degree of ionization of basic and acid amino acid groups affects the degree of

Table 5.2 Typical hydrocolloid emulsifiers and the related emulsions

Emulsifier	Emulsion type	References
Fish gelatin	Oil-in-water emulsion	Surh et al. (2006)
Fish gelatin/SDS	Oil-in-water emulsion	Surh et al. (2005)
Fish gelatin/whey protein isolate	Oil-in-water emulsion	Taherian et al. (2011)
Fish gelatin/sugar beet pectin	Multilayer emulsion	Zeeb et al. (2011)
Fish gelatin/gum arabic	Oil-in-water emulsion	Anvari and Joyner (2017)
Zein	Pickering emulsion	de Folter et al. (2012)
Zein/tannic acid complex particles	Pickering emulsion	Zou et al. (2015)
Zein/chitosan complex particles	Pickering emulsion	Wang et al. (2015)
Zein/propylene glycol alginate particles	Pickering emulsion	Dai et al. (2018)
Zein/gum arabic nanoparticles	Pickering emulsion	Li et al. (2018)
Zein/corn fiber gum	Pickering emulsion	Zhu et al. (2019)
Zein/propylene glycol alginate/rhamnolipid complex particles	Pickering emulsion (high internal phase)	Dai et al. (2019)
Zein/sodium caseinate/propylene glycol alginate	Pickering emulsion (high internal phase)	Sun et al. (2018)
Zein/tannic acid complex particles	High internal phase emulsion gel	Zou et al. (2019)
Whey protein/polysaccharides (locust bean gum, guar gum, xanthan gum, konjac gum)	Water-in-oil-in-water emulsion	Benichou et al. (2007)
Whey protein microgels/casein	Pickering emulsion	Chevallier et al. (2019)
Whey protein nanoparticles	Pickering emulsion	Wu et al. (2015)
Whey protein	Emulsion gel	Mantovani et al. (2016)
Whey protein microgel particles	Pickering emulsion	Sarkar et al. (2016)
Whey protein	Emulsion gel	Luo et al. (2019)
Sodium caseinate, whey protein isolate or isolated soy protein	Emulsion gel	Freire et al. (2018)
Casein	Emulsion gel	McIntyre et al. (2017)
Casein gel particles	Pickering emulsion	Wang et al. (2018a)
Casein/soy protein or casein/pea protein	Emulsion gel	Silva et al. (2019)
Casein/whey protein isolate	Emulsion gel	Balakrishnan et al. (2017)
β -lactoglobulin	Oil-in-water emulsion	Purwanti et al. (2016)
β -lactoglobulin	Nanoemulsion	Ali et al. (2016)
OSA modified quinoa starch granules	Water-in-oil-in-water Pickering emulsion	Marefati et al. (2015)
Guar gum	Water-in-oil-in-water emulsion	de Almeida Paula et al. (2018)

(continued)

Table 5.2 (continued)

Emulsifier	Emulsion type	References
Microcrystalline cellulose/soybean protein hydrolysate	Oil-in-water emulsion	Xu et al. (2016)
Nanofibrillated cellulose/guar gum/carboxy methyl cellulose	Oil-in-water emulsion	Golchoobi et al. (2016)
Locust bean gum/sodium caseinate	Water-in-water emulsion	Moschakis et al. (2018)
Ball-milling and OSA modified areca taro starch	Pickering emulsion	Liu et al. (2018)
Gelatinized native rice starch, waxy maize starch	Pickering emulsion	Kasprzak et al. (2018)
Pectin/zein complex	Oil-in-water emulsion	Piriyaprasarth et al. (2016)
Waxy corn starch/locust bean gum	Water-in-water emulsion	Murray and Phisarnchananan (2016)
Octenylsuccinate quinoa starch	Pickering emulsion gel	Li et al. (2019)
Quinoa starch waxy maize starch oat starch	Pickering emulsion	Saari et al. (2019)
Native corn (NCS), rice (NRS), wheat (NWS), and waxy corn (WCS) starch	Oil-in-water emulsion	Gómez-Luría et al. (2019)
Rice, wheat, potato, OSA potato starch	Pickering emulsion	Chen et al. (2019)
Wheat native starch and OSA waxy maize starch	Emulsion gel	Torres et al. (2017)

hydrophobicity. It is classified into four classes with different solubility behaviors, which are known as α -, β -, γ -, and δ -zein (Anderson and Lamsal 2011). Zein cannot be easily dissolved in either water or oil, but it is expected to fabricate colloidal particles by anti-solvent precipitation.

Zein colloidal particles have been extensively studied for preparation of Pickering emulsions. de Folter et al. (2012) found that the Pickering emulsions stabilized by unmodified zein colloidal particles were unstable to creaming. However, the improved stability of emulsions may be obtained by the stabilization of complex particles of zein and other biopolymers (e.g., proteins and polysaccharides) against coalescence and creaming through the modified wettability (Wang et al. 2015; Piriyaprasarth et al. 2016; Li et al. 2018). Zou et al. (2015) fabricated the zein/tannic acid complex colloidal particles based on hydrogen bonding to stabilize emulsions, which were extensively crosslinked to form a continuous network among and around the oil droplets and protein particles, leading to the formation of stable Pickering emulsion gels. Recently, the zein-propylene glycol alginate complex particles with a neutral wettability were fabricated to stabilize emulsions with a higher stability against coalescence (Dai et al. 2018). Zhu et al. (2019) fabricated the zein/corn fiber gum complex colloidal particle-stabilized Pickering emulsions, which were observed to have a gel-like network behavior. A neutral wettability was obtained

when the mass ratio of zein to corn fiber gum was 2:1, and the prepared Pickering emulsions exhibited better physical stability.

Zein-based complex particles have been also applied for stabilization of high internal phase emulsions or emulsion gels. Zou et al. (2019) fabricated the high internal phase emulsion gels with an oil content ranging between 72 and 87% (w/w) stabilized with the zein/tannic acid complexes at a particle concentration range of 0.7–1.4%. Lately, the zein-propylene glycol alginate-rhamnolipid complex particles were prepared with suitable three-phase contact angles to stabilize O/W Pickering high internal phase emulsions with an oil phase ratio of 75% (Dai et al. 2019). Similarly, Sun et al. (2018) fabricated the high internal phase Pickering emulsions stabilized by the ternary zein/sodium caseinate/propylene glycol alginate complexes at a volume concentration of as much as 80% oil. In a recent report, the Pickering emulsions at a high oil volume ratio (60%) were fabricated, which were effectively stabilized by the zein/gum arabic nanoparticles through the formation of a stable and thick oil–water interfacial layer to hinder agglomeration and Ostwald ripening (Li et al. 2018).

6.3 Casein

As a heterogeneous phosphorylated protein, casein comprises the major proteinaceous component of mammalian milk. Owing to the self-assembly and surface-active characteristics, casein is expected to stabilize O/W emulsions as an emulsifying agent based on electrostatic and steric stabilization mechanisms. The emulsifying capacity of casein products differs from their form: acid casein > micellar casein > rennet casein (Roman and Sgarbieri 2006). Tan and McGrath (2012) studied the emulsion morphology diagrams of the sodium caseinate/oil/water system. For the lowest emulsifier concentration, bridging flocculation was evident and the emulsions were very unstable. Increasing the sodium caseinate concentration enhanced the emulsion stability and promoted the existence of distinct individual oil droplets. The further increase in the sodium caseinate concentration caused a reduced stability, which was ascribed to depletion flocculation. Then the sodium caseinate self-assembly was initiated. The emulsion stability was again enhanced due to the formation of a three-dimensional protein network at sufficiently high sodium caseinate and/or oil concentrations.

In addition, the thermo-reversible gelation behavior was observed in the sodium caseinate-stabilized emulsions (Dickinson and Casanova 1999). Once heated to 30–40 °C, a concentrated liquid-like emulsion is converted into a flocculated emulsion gel that supports its own weight. The emulsion gel “melts” again slowly upon cooling, and the return to the original low-viscosity state is accelerated by stirring. Aggregated casein networks are commonly encountered in making yogurt and other fermented dairy products. The addition of lactic acid bacteria lowers the pH from 6.7 to lower than 4.5, resulting in a liquid-like dispersion of casein particles into a soft solid-like aggregated network. When the pH of sodium caseinate-

stabilized emulsions is lowered towards the protein's isoelectric point, a transition from the net repulsion to net attraction occurs, leading to droplet flocculation and then soft solid-like emulsions. Normally, the stiffness of the casein stabilized emulsion gels increases with the increasing oil content, as the oil droplets act as active fillers (i.e. the oil droplets are covered with proteins which are bound to the surrounding protein network) in the emulsion gels (Silva et al. 2019; Balakrishnan et al. 2017). It was reported that the sodium caseinate-stabilized emulsions showed a shear-thinning behavior as a result of a more structured system at pH 7.0, while at pH 3.0 the addition of laccase improved the emulsion stability by narrowing the size distribution and increasing the viscosity (Sato et al. 2015). Radford et al. (2004) studied the effects of alcohol and calcium on the sodium caseinate-stabilized emulsions, and found that the addition of calcium ions and/or ethanol resulted in a pronounced reduction in viscosity and the onset of Newtonian flow. Balakrishnan et al. (2017) fabricated the emulsion gels by heating the homogenized suspensions of micellar casein mixed with sunflower oil at various pH (5.8, 6.0, and 6.3) and oil weight fractions (5, 10, and 15%). The gel stiffness increased with the decreasing pH and the increasing oil ratio. The gel stiffness did not change significantly after replacing up to 40% casein by whey protein at pH 5.8 or 6.0, but decreased significantly at pH 6.3. However, the addition of a small amount of casein into whey protein microgel stabilized Pickering emulsions effectively improved the heat stability of the emulsions by competitive adsorption at the interface (Chevallier et al. 2019). McIntyre et al. (2017) prepared the casein-based emulsion gels with milk fat or rapeseed oil at high (774 mg/100 g) or low (357 mg/100 g) calcium levels. Compared with the low-calcium emulsion gels, the high-calcium gels were significantly softer and showed the highest disintegrated rate during the simulated gastric digestion. The fatty acid releases were similar for all the emulsion gels made from milk fat, while a higher lipolysis was found in the high-calcium emulsion gels made from rapeseed oil. Silva et al. (2019) reported that micellar casein could be replaced by plant proteins (e.g. soy protein and pea protein) while maintaining the same emulsion gel stiffness.

Sodium caseinate has been found to facilitate the formation of the high internal phase Pickering emulsions stabilized by the zein/sodium caseinate/propylene glycol alginate complexes (Sun et al. 2018). The casein gel particles were also fabricated by covalently genipin crosslinking of a protein network with the self-associated sub-micelles or calcium induced casein micelles to stabilize Pickering emulsions (Wang et al. 2018a). The oil droplets stabilized by these particles exhibited higher stability against flocculation and creaming, compared to those stabilized only by sodium caseinate.

6.4 *Whey Protein*

Whey protein has been widely used in food industry as an emulsifier, which consists of β -lactoglobulin (~65%), α -lactalbumin (~25%), bovine serum albumin (~8%),

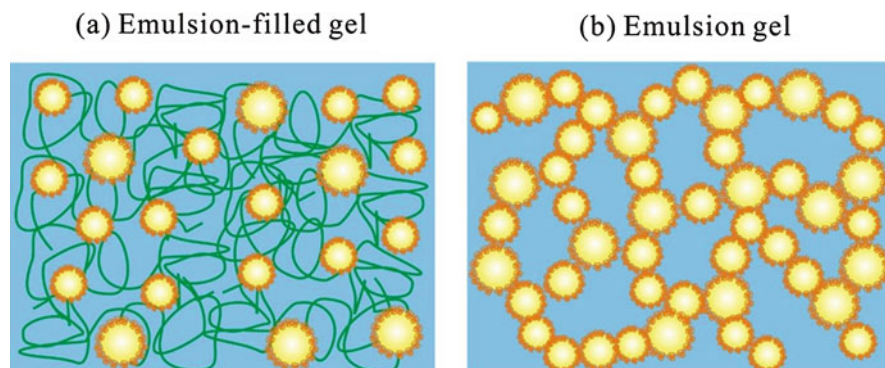


Fig. 5.7 Schematic presentation of (a) an emulsion-filled protein gel and (b) a protein-stabilized emulsion gel. Yellow circle, oil; small red circle, protein; light blue, water; green curve, protein network

and immunoglobulins (Morr and Ha 1993). Compared to casein, whey protein can be used over a wider pH range since its solubility goes through a minimum at the isoelectric point at pH close to 5. This makes whey protein applicable to acidic environments where caseins cannot be used, especially at pH below 4.5. However, heat treatment has a significant effect on the properties of the whey protein-stabilized emulsions, since the non-covalent interactions maintaining the secondary and tertiary structures of the globular protein would be broken by thermal energy. It has been extensively investigated about the stability of the whey protein-stabilized emulsions in terms of the effect of heating. Euston et al. (2000) found that the interactions between the adsorbed protein at the emulsion droplet surface and the non-adsorbed heat denatured protein in the continuous phase were the main cause of aggregation, and the non-adsorbed protein acted as a “glue” holding the aggregated emulsion droplets together.

Whey protein has been used for preparation of emulsion gels as well, due to its characteristic heat-induced gelling property (Dickinson 2012). The major whey protein in cow’s milk is β -lactoglobulin, which denatures and aggregates upon heating to a temperature of 70 °C, like many other globular proteins. At the molecular level, this aggregation and subsequent gelation are a result of the developed hydrophobic interactions between the exposed non-polar regions of the unfolded β -lactoglobulin molecules. The sulfhydryl-disulfide interchange leading to covalent crosslinking may also improve the evolving network structure. Therefore, this complex colloidal system may exist as both an emulsion and a gel, which can be expressed as “emulsion gel” for understanding. To specify more precisely the properties of such protein-based systems, two structural arrangements can be distinguished: (a) the emulsion-filled protein gel and (b) the protein-stabilized emulsion gel. As shown in Fig. 5.7a, the emulsion-filled protein gel is a protein gel matrix within which emulsion droplets are embedded. It is a kind of particle-filled solid due to the network properties of the spatially continuous matrix in charge of its solid-like rheological properties. The protein-stabilized emulsion gel is shown schematically in

Fig. 5.7b. It is a type of particulate gel, and its rheological properties are mainly determined by the properties of the network of aggregated emulsion droplets.

Above a critical concentration, whey protein can be crosslinked to form a three-dimensional gel network by heating, acidification or enzymatic treatment. The whey protein emulsion gel structure can be modified by varying pH, droplet size, ionic strength, and temperature. Mantovani et al. (2016) studied the effect of pH on cold-set gel formation by acidification of emulsion gel (30% oil and 5% non-heated whey protein isolate (WPI)) and emulsion-filled gel (emulsion dispersed in heat-treated whey protein solution), and found that stronger gel strength was obtained at a pH near the isoelectric point of whey protein because of protein aggregation promoted by lower acidification rate and electrostatic repulsion. Guo et al. (2017) investigated the effect of gel structure and rheology on the intestinal digestion of canola oil dispersed within O/W emulsions gelled with WPI. The softer and microstructurally homogeneous gels were obtained at lower salt concentrations. The rate of lipid digestion increased due to the looser, less spatially heterogeneous protein matrix, in comparison to the firmer gels. Overall, the extent and rate of lipid digestion were modified by the strength and microstructure of the WPI-stabilized emulsion gels, which may be used to produce emulsion-based food products. For example, the emulsion gels containing ω -3 fatty acids and condensed tannins were fabricated with WPI for potential use of healthier fat replacers (Freire et al. 2018). Luo et al. (2019) encapsulated capsaicinoids in whey protein emulsion gels, and studied the structural relationship with the in-mouth breakdown behavior. A greater hardness led to a smaller bolus particle size, but a higher degree of fragmentation caused greater surface exposure during mastication.

Besides, soft whey protein microgel particles used as an emulsion stabilizer can show the combined advantages of biocompatibility and an increased stability against coalescence. Wu et al. (2015) prepared the Pickering O/W emulsions stabilized by WPI nanoparticles in the size range of 200–500 nm, which exhibited good stability against coalescence. Sarkar et al. (2016) designed the Pickering O/W emulsions using whey protein microgels by a facile route of heat-set gel formation followed by mechanical shear, and studied the influence of heat treatment on the emulsions stabilized by these particles. In addition, the whey protein microgel particles could also act as a stabilizer for waxy corn starch/locust bean gum water-in-water emulsions (Murray and Phisarnchananan 2016).

6.5 β -Lactoglobulin

β -Lactoglobulin, a dominant globular protein found in whey fraction, possesses a remarkable emulsifying property, which is commonly used in the formulation of food emulsions. β -lactoglobulin has showed great potentials as a transport vehicle for hydrophobic compounds, since it can bind hydrophobic vitamins and fatty acids in inner cavities (Kimpel and Schmitt 2015). Moro et al. (2013) studied the effects of heat treatment on the emulsifying properties of β -lactoglobulin. For a shorter time

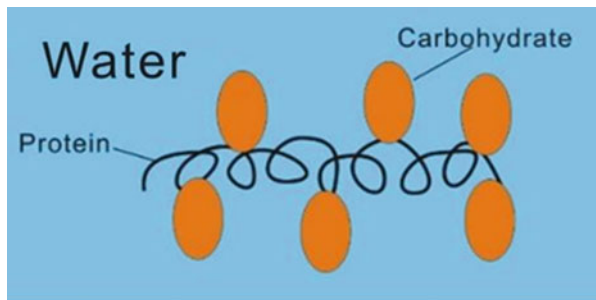
period of heating, both the foamability and foam stability were improved, but the emulsifying property diminished. However, after 10 min of heating at 85 °C, both the foaming and emulsifying properties were impaired. Purwanti et al. (2016) studied the unheated and heat-aggregated β -lactoglobulin stabilized clove oil-in-water emulsions and limonene-in-water emulsions by microchannel emulsification. The monodisperse emulsion droplets were consistently produced using unheated or heat-aggregated β -lactoglobulin with concentrations from 0.5 to 3% (w/w) at pH 7. Ali et al. (2016) fabricated the β -lactoglobulin stabilized biocompatible nanoemulsions prepared by high-pressure homogenization. The nanoemulsions with 1 wt% β -lactoglobulin and with 5 wt% Miglyol 812 (a mixture of medium chain triglycerides) had a relatively small particle size (\sim 200 nm) and a low polydispersity, when a homogenization pressure of 100 MPa was applied for 4 cycles. These nanoemulsions were made stable for at least 30 days. However, the emulsification capacity of β -lactoglobulin was reduced at higher homogenization pressures (200 MPa and 300 MPa).

7 Polysaccharides

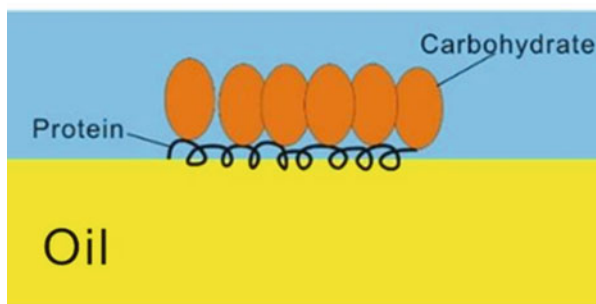
7.1 Gum Arabic

Gum arabic was once a kind of hydrocolloids widely used in food industry, and now there is still 40–50 thousand tons per year consumed in the worldwide market. It helps to stabilize the flavor and essential oils in production of soft drinks or concentrated juices. Gum arabic (*A. senegal*) is a complex branched heteropolyelectrolyte with a backbone of 1,3-linked β -galactopyranose units and side-chains of 1,6-linked galactopyranose units terminating in glucuronic acid or 4-O-methylglucuronic acid residues. There are three different fractions separated from gum arabic, namely, arabinogalactan (\sim 90% of total mass), arabinogalactan protein (\sim 10%), and glycoprotein (\sim 1%) (Randall et al. 1989). Gum arabic is a polysaccharide emulsifier naturally conjugated with protein. The structure of this protein-polysaccharide complex is known as the “wattle blossom” model (Fig. 5.8), in which the hydrophobic protein moieties adsorb onto the oil droplet surface, and the covalently attached hydrophilic carbohydrate blocks protrude into the aqueous phase against droplet flocculation and coalescence (Dickinson 2008). Though it serves as a stabilizer to form a thick steric stabilizing layer and protect the flavor and essential oils in emulsion products at intermediate pH values, high ionic strengths or high temperatures, gum arabic shows a lower affinity for the oil-water interface than most other surface-active biopolymers. The α -tocopherol encapsulated nanoemulsions with gum arabic as an emulsifying and stabilizing agent were fabricated through solvent-displacement technique (Moradi and Anarjan 2018). The monomodal size distribution was successfully obtained with a mean particle size of 10.01 nm, 49.46 nm, and 171.2 nm for the emulsions prepared with 0.05%, 0.1%, and 0.15% gum arabic, respectively. Hu et al. (2019) reported that gum arabic

Fig. 5.8 Schematic representation of the wattle blossom model of gum arabic (a) in solution and (b) at the oil-water interface. Hydrophilic carbohydrate blocks and the backbone chain of hydrophobic protein were illustrated



(a)



(b)

enriched with trace elements (Zn^{2+} , Fe^{3+} , Fe^{2+}) had good emulsion stability as the molecular weight and arabinogalactan protein content increased, in comparison to the control gum arabic. Atgié et al. (2018) found that the protein-rich species of gum arabic irreversibly adsorbed as monolayers at the oil–water interface, and the absorbed amount drastically increased with both the decreasing ionic repulsions and the increasing gum concentration. However, those changes corresponded to only minor composition changes in the adsorbed layer, suggesting a significant role of controlling the interfacial density in a rational design of gum arabic-based formulations.

7.2 Pectin

Pectin is another class of hydrocolloid with a fascinating emulsifying character, while its emulsifying property differs depending on the varieties of plant sources. For example, citrus and apple pectin can form gels at low pH and serve as thickening agents but not effective emulsifying agents, while sugar beet pectin is normally used

as an excellent emulsifying agent owing to the protein moiety, acetyl groups, and highly branched polysaccharide structures, and it can form a thick hydrated layer that may prevent droplets from flocculation and coalescence through electrostatic and steric repulsive forces. Williams et al. (2005) found that the emulsifying property of sugar beet pectin was affected by the proportion of ester groups, the accessibility of the protein and ferulic acid groups to oil droplet surface, and the molecular mass distribution of the fractions. However, no simple relationship existed between the emulsifying property and the protein or ferulic acid content. Funami et al. (2011) reported that the emulsifying property of the deproteinized sugar beet pectin with a protein content ranging from 5 to 0.5% became worse than that of the untreated pectin. Siew et al. (2008) reported that an increase in the protein content (12% higher than the average) of sugar beet pectin would help adsorb onto the oil droplets. Chen et al. (2016a) observed a significant decrease in the droplet size of the sugar beet pectin stabilized emulsions, as the protein content of sugar beet pectin increased from 0.5 to 3%.

7.3 Galactomannan

As the most commonly used plant polysaccharides, galactomannans belong to the legume family consisting of β -(1-4-) linked D-mannan backbone by substitution of α -(1-6-) linked D-galactose stubs for certain mannose residues. Locust bean gum and guar gum are high molecular weight galactomannans used as food additives, since no significant proportion of hydrophobic groups presents in the carbohydrate structure. This type of hydrocolloid can be assumed to be used for modifying the rheological properties of the continuous aqueous phase between dispersed particles or droplets. To date, the surface and interfacial properties of guar gum and locust bean gum have been extensively studied (Reichman and Garti 1991).

It was reported that the emulsions with similar droplet size distributions showed similar stability when crude, purified and bipurified guar gums were used to prepare emulsions under similar conditions (Garti and Reichman 1993). However, the emulsions made from the guar gum with a proteinaceous-rich fraction had larger droplets and relatively low stability with the fastest coalescence rate upon dilution. Later, Garti and Reichman (1994) found a similar degree of surface activity and emulsification ability when the guar gum was purified down to 0.8% protein. Thus, it is conceivable that the slight hydrophobicity of the polymannose backbone may contribute to some emulsion stabilizing properties.

In a recent study, guar gum was used to fabricate W/O/W double emulsions for improving the heat stability of anthocyanins at pH 4.0 (de Almeida Paula et al. 2018). In addition, various levels of guar gum (0.5, 1.0, and 1.5%) were used as a fat substitute to prepare low-fat meat emulsions. The reduction of fat by incorporation of guar gum was found to increase the emulsion stability and cooking yield but decrease the penetration force (Rather et al. 2017). To develop a new low-fat mayonnaise formulation, nine mayonnaise samples containing different

compositions of nanofibrillated cellulose, guar gum, and carboxymethyl cellulose were compared to the commercial low-fat mayonnaise with 30% fat (Golchoobi et al. 2016). In addition, the water-in-water emulsions containing sodium caseinate and locust bean gum have been also fabricated as potential functional ingredients to mimic fats (Moschakis et al. 2018).

7.4 *Microcrystalline Cellulose*

Microcrystalline cellulose (MCC) is among the most common cellulose derivatives in food industry (Nsor-Atindana et al. 2017). It is a hydrocolloid without solubility in water but adsorbs mechanically at the oil–water interface (Garti and Reichman 1993). The cellulose crystallites are claimed to build a network made from the majority of the particles being less than 0.2 μ m. The formed colloidal network of the free MCC thickens the water phase between oil globules and provides effective stabilization against their subsequent coalescence (Milani and Maleki 2012).

When colloidal MCC is dispersed in water, it can be expected to simulate the fat-induced rheology owing to the inherent properties in food applications such as baked products, frozen desserts, mayonnaise, gravies, and sauces. For example, an emulsion with 60% soybean oil showed similar stability and rheology characteristics, compared to the emulsion containing 1–1.5% colloidal MCC and 20% soybean oil (Imeson 2011). The use of MCC as a fat substitute gives a rich creamy texture in low-fat sauces and dressings, because of the insoluble material to mimic fat. MCC may be used alone or in combination with other polysaccharides in ice cream, which is expected to increase the solid content and improve the stability and ice rheology (Nsor-Atindana et al. 2017).

In general, crystals of cellulose within micro/nanoscale dimension (MCC/NCC) have been commonly applied for preparation of Pickering emulsions. Kalashnikova et al. (2011) confirmed that Pickering O/W emulsions could be effectively stabilized by bacterial cellulose nanocrystals for several months if the particles were properly dispersed. The colloidal MCC particles (11% colloidal MCC combined with 1% sodium carboxymethylcellulose) could also form a network around the emulsified oils and then act as a stabilizer of O/W emulsions and W/O/W multiple emulsions (Jia et al. 2014), in which MCC not only thickened the continuous phase between the droplets, but also provided a mechanical barrier to prevent oil droplet coalescence (Dickinson 2013). In another study, the microrheological property of curcumin emulsions was changed by the addition of MCC, as evidenced by a transition from the viscous to viscoelastic behavior of the emulsions. The freeze-thaw stability of the emulsions was significantly improved by MCC, which was attributed to the enhanced repulsive steric forces between the curcumin droplets. In addition, stearylated microcrystalline cellulose was recently reported to fabricate high internal phase Pickering emulsions with the highest internal phase ratio of 89% (Pang et al. 2018).

7.5 Starch

Starch (including hydrophobically modified starch) is an abundant, inexpensive, and natural food ingredient, while the natural variation regarding the size, shape, and composition of starch granules normally occurs among its numerous botanical sources. For native starch, it cannot achieve adsorption to the oil–water interface as an emulsifying agent. Therefore, starch has been modified to become more suitable for emulsion stabilization. Physical modifications, including milling, non-solvent precipitation, ultrasonication, high-pressure treatment may be applied to reduce the size of starch. Decreasing the particle size of starch often relates to the increased storage stability of its Pickering emulsions. Octenyl succinic anhydride (OSA) modification is the most commonly used chemical modification method, which improves the hydrophobicity of starch. OSA modified starch with a degree of modification <3%, E1450, is a well-established food ingredient with no specific limitations on its use (Timgren et al. 2011). The Pickering emulsion gels were formed by stabilization of octenylsuccinate quinoa starch granules at an oil fraction ranging from 50 to 70% (Li et al. 2019). Liu et al. (2018) compared the stability of soybean oil-in-water Pickering emulsions stabilized by different areca taro starches (native starch, OSA esterified starch, ball-milled starch, and compound modified starch with ball-milling and OSA), and found that the compound modified starch showed strong surface activity and high emulsion viscosity, leading to the best emulsifying capacity and stability. Nevertheless, it should be noted that the amylose/amylopectin ratio also affects the emulsion properties. Lu et al. (2018) reported that the milled high-amylose maize starch particles had the best stabilization ability, followed by milled normal maize starch particles. Kasprzak et al. (2018) screened a series of commercially available food starches, and found that a waxy rice starch showed the O/W emulsifying ability following gelatinization. In addition, the OSA modified quinoa starch granules were also reported to be used to make W/O/W double emulsions with solid or liquid shea oil (Marefati et al. 2015). The double emulsions were freeze-dried and then rehydrated for emulsion reformation, which had a similar droplet size to that of the initial emulsion, suggesting a high process stability.

8 Protein-Polysaccharide Conjugates

Numerous studies on the emulsifying properties of protein-polysaccharide conjugates have been published in the last few years. A conjugate is the material made from a protein covalently linked by a polysaccharide via Maillard reaction, in which temperature, humidity, and concentration of ingredients need to be carefully controlled. Maillard reaction is a series of non-enzymatic browning reactions that occur naturally between the reducing end of a sugar and amino acids. The functional properties of protein and polysaccharide can be combined through Maillard reaction

from the production of a novel protein-polysaccharide conjugate, which may be expected to result in an enhanced protein functionality both as an emulsifier and a stabilizer.

Several methods including wet heating, dry heating, and molecular crowding are often used to induce Maillard reaction between proteins and polysaccharides. For dry heating, to ensure sufficient contact, the powders of the protein and polysaccharide are obtained by freeze-drying the mixture firstly dispersed in water, and then heated in an apparatus at the controlled time, temperature, and relative humidity. Wet heating can also be used to prepare protein-polysaccharide conjugates by heating the ingredients present in a buffer solution for hours. It is considered as a more efficient method with the improved control over the reaction advancement, in comparison to the dry heating technique. However, the concentration of reactants needs to be increased for a higher glycation level, as molecular crowding is of necessity for Maillard reaction under less adverse treatments in aqueous solutions (Perusko et al. 2015; Weng et al. 2016). In the presence of high concentrations of biological macromolecules, the reaction follows the excluded volume theory, and the crowded environment promotes the conjugation between protein and polysaccharide. In addition, the extent of protein aggregation can potentially be minimized in the macromolecular crowding environment. Recently, ultrasound has been applied to facilitate the Maillard reaction. It was reported that the conjugates obtained by the ultrasound treatment had better emulsifying properties, compared to those prepared by classical heating (Xue et al. 2017; Chen et al. 2016b; Liu et al. 2016). Stanic-Vucinic et al. (2013) found that high-intensity ultrasound efficiently promoted the glycation of β -lactoglobulin by Maillard reaction, and the obtained conjugates possessed the improved antioxidant capacity, with a minor influence on protein's secondary and tertiary structures.

Table 5.3 illustrates some studies involving the conjugates from proteins (e.g., whey protein, casein, β -lactoglobulin, and soy protein), and polysaccharides (e.g., guar gum, pectin, and dextran). High molecular weight conjugates possess the properties of protein, strongly adsorbing at the surface of oil droplets, as well as the hydrophilic properties of polysaccharide, being highly solvated by the aqueous medium. The conjugation between proteins and polysaccharides may provide much more improved steric stabilization for emulsion droplets, as illustrated in Fig. 5.9. As the molecular weight of the polysaccharide moiety sufficiently increases, a thicker stabilizing layer can be formed by the conjugate in an emulsion. Therefore, the well-prepared protein-polysaccharide conjugates may show the substantially improved emulsifying and stabilizing properties compared to native proteins (Sivapratha and Sarkar 2018).

Great concerns have been also raised by the presence of a protein and polysaccharide as naturally occurring substances with the emulsifying capacity produced by Maillard reaction. Cirre et al. (2014) conducted a heat-induced maturation treatment for corn fiber gum in the solid state, which induced a reduction in the solubility and incensement in the aggregation of the proteinaceous component. The emulsification performance and stability of the matured samples were greatly improved, in comparison with the control gum. A 3-fold increase in the proportion of the adsorbed

Table 5.3 Formation, characterization, and functionality of protein-polysaccharide conjugates obtained via Maillard reaction

Protein	Polysaccharide	Reaction condition	Characterization methods	Main results	References
Whey protein	Guar gum	Wet heating, 50 or 70 °C, 15 min	SDS-PAGE (sodium dodecyl sulfate polyacrylamide gel electrophoresis)	Cumin seed oil (CSO) nanoemulsions were prepared using preheated 10% WPI and 0.2% guar gum in aqueous phase, and the mixture of CSO and corn oil (30:70) as oil phase.	Farshi et al. (2019)
Deamidated wheat gluten	Citrus pectin or maltodextrin	Dry heating, 80 °C, RH (relative humidity) 79%, 24 h	OPA (o-phthalaldehyde), SDS-PAGE, FTIR (Fourier transform infrared), CD (circular dichroism)	Conjugates prepared by dry heating deamidated wheat gluten/maltodextrin (1/1) for 9 h showed the best emulsifying properties.	Wang et al. (2019)
Whey protein	Pectin	Dry heating, 80 °C, RH 79%, 6–168 h	SDS-PAGE, HPSEC (high-pressure size exclusion chromatography)	Solubility and emulsion stability were improved.	Wefers et al. (2018)
Casein	Carrageenan	Dry heating, 60–80 °C, RH 79%, 6–72 h	OPA, Color, FTIR, fluorescence measurements	Conjugates obtained at 60 °C for 24 h showed the best emulsifying activity and stability.	Qiu et al. (2018)
Bovine serum albumin	Sugar beet pectin	Dry heating, 85 °C, RH 79%, 5 h	SDS-PAGE, Color, GPC (gel permeation chromatography)	Covalent conjugates exhibited good emulsion stability under the extreme environmental conditions.	Chen et al. (2018)
Rice protein	Dextran	Wet heating, pH 12, 80–100 °C, 10–30 min	TNBS (2,4,6-trinitrobenzene sulfonic acid), HPSEC, SDS-PAGE, FTIR	Emulsifying activity and stability were increased by factors of 1.79 and 2.2, respectively.	Cheng et al. (2018)
Egg-white lysozyme	Guar gum	Dry heating, 60 °C, RH 80%, 10 days	SDS-PAGE, Color, GPC, FTIR	Emulsion capacity and stability were significantly improved.	Hamdami et al. (2018)
Sodium caseinate	Locust bean gum	Dry heating, 80 °C, RH 79%, 4 days	SDS-PAGE, Color, FTIR	Conjugates produced at 80 °C after 24 h showed good emulsifying properties.	Barbosa et al. (2018)

(continued)

Table 5.3 (continued)

Protein	Poly saccharide	Reaction condition	Characterization methods	Main results	References
Whey protein isolate (WPI)	Citrus pectin	Closed-cavity rheometer, 80–140 °C, 0.75–10 min	HPSEC, fluorescence measurements	A novel Maillard reaction method was applied to highly concentrated WPI-highly methylated citrus pectin blends at elevated temperatures.	Koch et al. (2017)
Soy protein isolate	Dextran	Dry heating, 60 °C, RH 79%, 8 days	SDS-PAGE, OPA, FTIR	Oil droplet size was decreased, and emulsion stability was improved.	Boostani et al. (2017)
Casein hydrophobic peptide (CHP)	<i>Acacia seyal</i> polysaccharide	Dry heating, 60 °C, RH 75%, 3 days	TNBS, HPSEC	Conjugates prepared from <i>A. seyal</i> polysaccharide and CHP with a degree of hydrolysis of 1.5% presented the best emulsifying properties.	Hou et al. (2017)
Soy protein isolate (SPI)	Soy hull hemi-cellulose (SHH)	Dry heating, 60 °C, RH 75%, 7 days	Color, FTIR, free amino acids	Optimized SHH-SPI conjugates exhibited the substantially improved emulsification capacity.	Wang et al. (2017)
WPI	Maltodextrin	Dry heating, 80 °C, RH 79%, 3 h	OPA	Emulsifying and colloid stabilizing properties were improved.	Ding et al. (2017)
Canola protein isolate	Gum arabic	Wet heating, pH 7.0, 90 °C, 15 min	SDS-PAGE, HPSEC	Conjugate-stabilized emulsions showed smaller droplet size, lower creaming index, and higher resistance to pH and heat.	Pirestani et al. (2017)
β -lactoglobulin	Gum <i>Acacia Seyal</i>	Dry heating, 60 °C, RH 79%, 0–48 h	TNBS, SDS-PAGE	Emulsion stabilities against storage, pH, temperature, and salt were improved.	Bi et al. (2017)
β -lactoglobulin	Chitosan	Wet heating, pH 6.0, 40 °C, 0–7 days	SDS-PAGE, fluorescence measurements	Emulsifying properties were improved.	Mengfbar et al. (2017)

Soy β -conglycinin	Dextran	Macromolecular crowding, pH 7.0, 95 °C, 6 h; Dry heating, 65 °C, RH 75%, 96 h	SDS-PAGE, TNBS	Degree of conjugation grafting carried out in macromolecular crowding environment was generally higher than that produced by dry heating method.	Weng et al. (2016)
Buckwheat protein isolate	Dextran	Ultrasound-assisted wet heating, 70 °C, 80 min; Wet heating 70 °C, 40 h	FTIR, CD, fluorescence measurements	Emulsifying properties of the conjugates obtained by the ultrasound treatment were improved, compared to those obtained by classical heating.	Xue et al. (2017)
Peanut protein isolate (PPI)	Maltodextrin	Ultrasound-assisted wet heating, pH 7.0, 70 °C, 10–100 min	OPA, SDS-PAGE	High-intensity ultrasound promoted the production of glycosylated PPI.	Chen et al. (2016b)

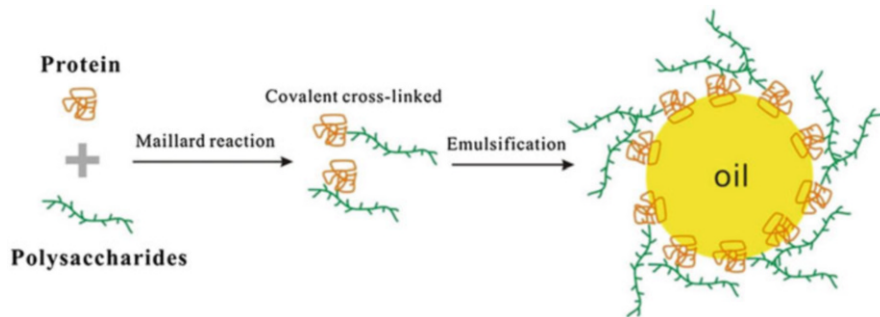


Fig. 5.9 Schematic representation of Maillard reaction between proteins and polysaccharides. The formed conjugates are used to improve stabilization of emulsions

fraction onto the oil–water interface accounted for the improved emulsification. As for okra hydrocolloid mucilage, it has both proteins and characteristic slimy polysaccharides. Heating at 100 °C for 6 h resulted in the conjugates that showed better emulsifying property than the ones formed between okra polysaccharides and bovine serum albumin (Temenouga et al. 2016). Lately, brea gum, which is an exudate from *Cercidium praecox* tree, was purified and subjected to thermal treatment at 110 °C for 24, 48, 72, and 96 h, respectively. The thermally treated brea gum presented changes in the molecular mass of its protein fractions and in its color parameters as a result of non-enzymatic browning reactions. The modifications in the gum structure produced an increase in its surface activity and improved its emulsifying/stabilizing capacity, leading to corn oil-in-water emulsions stable for several months (Castel et al. 2018).

9 Applications in Food Industry

The hydrocolloid stabilized emulsions have showed a number of applications in the food industry, such as dairy products, meat products, beverages, etc. (Fig. 5.10). Beverage emulsions are a unique class of emulsions, which are consumed in a highly dilute form. The emulsions in both the concentrate and diluted forms must be stable at least for 6 months. Gum arabic is the most widely used emulsifier as well as a stabilizer in beverage emulsions. The most accepted alternative to gum arabic for beverage emulsions is modified starches, whose lipophilic and hydrophilic groups can be balanced by modifications (Tan 2004). There are other hydrocolloids with good emulsifying properties to be used in beverage emulsions, for example, locust bean gum. In ice cream, hydrocolloids have been applied for various functions, especially as a stabilizer, fat replacer, and cryoprotectant (Javidi and Razavi 2019). Structurally, it consists of a complex matrix of fat globules, ice crystals, air bubbles, and a continuous phase of unfrozen water with dissolved sugars, proteins, and salts (Daw and Hartel 2015). Gelatin almost exclusively serves as a stabilizer in the ice



Fig. 5.10 Major applications for hydrocolloid emulsifiers in food industry

cream industry, but has gradually been replaced by the polysaccharides of plant origin due to their increased effectiveness and reduced cost. Blends containing locust bean gum, guar, and carrageenan are excellent stabilizing systems for ice cream. Sausages are made of a fine homogenate by adding water and salt into chopping meat, in which the dispersion and emulsification of pork fat is further achieved. Solubilization of muscle protein is associated with the interactions with salt solutions during blending of meat. Then, a stable emulsion is formed due to the formation of a surrounding layer of the salt soluble proteins at the surface of the released fat. In sausage products, more myofibrillar proteins are extracted, thus heat treatment can contribute to the formation of a stronger gel. Sodium caseinate, soy protein isolate, guar gum, xanthan, gellan gum are commonly used in meat products as emulsifiers.

Due to the high calorific value and/or the fat-related health problems caused by high-fat diets, the demand for reduced-fat counterparts in food products has been developed in recent years (Azeredo et al. 2019). Some studies of fat replacement have been performed using different hydrocolloids in various products, such as ice cream, mayonnaise (Golchoobi et al. 2016), sausages (Pintado et al. 2018). Several structuring approaches have been reported to mimic the fat texture. Emulsion gels have been fabricated by casein, whey protein isolate, soy protein isolate as emulsifiers (Freire et al. 2018). Double emulsions (W/O/W) have been fabricated to maintain the contact area between fat and the oral surface in the mouth. Pickering emulsions have been successfully stabilized by zein, starch granules, cellulose crystals, whey protein microgels, crosslinked casein gel particles as potential fat replacers (Javidi et al. 2019; Wang et al. 2018b). Nanoemulsions are more stable against creaming, sedimentation, coalescence, and flocculation, and have higher surface area and more free energy, so they are suitable carrier systems. Recent researches have shown that the nanoemulsions stabilized with proteins were more stable than those stabilized by low molecular weight surfactants due to the formation

of an elastic film by proteins, which can inhibit coalescence of droplets in the dispersed phase. In addition, the bioactive encapsulated nanoemulsions have been prepared by stabilization of hydrocolloids, such as β -lactoglobulin (Ali et al. 2016), pectin/whey protein complexes (Esfanjani et al. 2015; Gharehbeqlou et al. 2019).

10 Future Prospects

Over the last decade, a growing number of studies have focused on the characterization of the emulsifying properties of food hydrocolloids, leading to a fundamental understanding of the mechanisms of their interfacial functionalities. Apart from the known hydrocolloid emulsifiers, more and more naturally extracted biopolymers will be explored as a novel candidate for applications in foods, inspired by the consumer preference for clean label ingredients. Many studies have also shown that the protein-polysaccharide conjugates induced by Maillard reaction may present the improved emulsifying property compared to the single components, indicating the potentials to be used in beverages and dairy products. However, the main challenge for developing such novel emulsifiers is to select a conjugated fraction with high functionality in emulsions under a certain environmental condition for the desirable formulated products. Therefore, in future more studies are needed to understand the relationship between the conjugate structures and functional properties before use in practical applications.

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