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21 **Abstract**

22 Background

23 Emulsion gels are a class of soft solid-like materials. These composite materials are structurally  
24 either a polymeric gel matrix into which emulsion droplets are incorporated (emulsion-filled gels),  
25 or a network of aggregated emulsion droplets (emulsion particulate gels). Emulsion gels are  
26 increasingly used in pharmaceuticals, cosmetics and food industries.

27 Scope and Approach

28 This article reviews fabrication methods of emulsion gels, and describes factors that influence gel  
29 properties and functionality. Effect of polymer-surfactant interactions on the rheology of emulsion  
30 gel systems is explained. Then, irreversible and reversible clustering of oil droplets as the basis of  
31 making emulsion particulate gels is deliberated.

32 Key Findings and Conclusions

33 Oil droplets depending on their interfacial composition act as either active or inactive fillers in an  
34 emulsion-filled gel. Actively functioning oil droplets can increase gel modulus, whereas, inactive  
35 oil droplets typically weaken gel texture. Interactions between surfactants and polymers, which  
36 influences filler affinity to gel matrix, have significant consequences on emulsion gel rheology.  
37 For protein-based emulsion gels, surfactant may also influence proteins unfolding and aggregation.  
38 In situ gelation of an emulsion can be triggered by environmental factors such as temperature  
39 changes during processing and storage or by physiological stimuli such as acidic pH in the  
40 stomach. The clustering approach, which is used to form emulsion particulate gels may be utilized  
41 to control digestibility of lipids in the gastrointestinal tract. The capability of encapsulating two or

42 more different lipophilic components within a single delivery system may be achieved via  
43 heteroaggregation technique.

44 *Keywords:* Emulsion gel; Aggregated droplets; Filler particle; Adsorbed polymer.

## 45 **1. Introduction**

46 Oil-in-water emulsions have been widely utilized in various domains such as food, pharmaceutical,  
47 cosmetic, and paint **industries** owing to their ability to transport or solubilize hydrophobic  
48 components in a water continuous phase (Budai-Szucs, 2008; Leal-Calderon, Schmitt, & Bibette,  
49 2007). However, emulsions are thermodynamically unstable systems and attempt to revert back  
50 into separate water and oil phases over time via various physicochemical mechanisms, including  
51 coalescence, gravitational separation, flocculation, Ostwald ripening and phase separation  
52 (McClements, 2014; McClements, Decker, & Weiss, 2007). This hinders their more widespread  
53 application. For example, in pharmacy and medicine, emulsions are limitedly used for oral and  
54 parenteral administration of drugs due to their unpredictable drug release profiles and possible  
55 toxicity that arise from emulsion instability (Budai-Szucs, 2008; Eccleston, 2013; Sarkar, 2009).

56 The stability of emulsion can be greatly improved by confining oil droplets within a three-  
57 dimensional solid-like aqueous network (hydrogels). Formation of a hydrogel network  
58 immobilizes droplets within the gel structure, thus preventing flocculation and coalescence  
59 (Eccleston, 2013). Hydrogels, on the other hand, may be per se utilized as delivery systems owing  
60 to their ability to protect active ingredients from hostile environments and to deliver them in  
61 response to environmental stimuli such as alterations in temperature and pH (Komaiko &  
62 McClements, 2015; Subirade & Chen, 2008). In the food industry, a fundamental advantage of  
63 utilizing hydrogels is that they can stabilize food texture, which is a desirable feature in

64 manufacturing food products (Subirade & Chen, 2008). Nonetheless, hydrogels are not proper  
65 carriers for delivery of hydrophobic compounds (Nayak, Olatunji, Bhusan Das, & Vladislavljevic,  
66 2016). Fabrication of a composite system, named “emulsion gel” or “emulgel can provide the  
67 advantages of both emulsions and hydrogels, i.e., the ability to solubilize both hydrophobic and  
68 hydrophilic components and also good thermodynamic stability (Torres, Murray, & Sarkar, 2016).  
69 As a consequence, emulsion gels can act as dual control release systems (Alexander et al., 2013).  
70 These composite materials can be considered as a network of cross-linked polymers into which  
71 droplets are embedded (described as emulsion-filled gels), or as a network formed from flocculated  
72 droplets. The latter is a type of particulate gel (Dickinson, 2012, 2014). However, distinguishing  
73 among cross-linked biopolymer molecules and flocculated droplets is not always easy for some  
74 real systems such as food emulsion gels and their composite structure is considered as a hybrid  
75 network fabricated from a combination of both these idealized models of structuring (Dickinson,  
76 2014; Geremias-Andrade, Souki, Moraes, & Pinho, 2016).

77 Emulsion gels can be produced with a wide range of rheological properties, which depend on a  
78 number of intrinsic factors such as the nature of interactions between the components, droplet  
79 volume fraction, and matrix stiffness (Dickinson, 2014; Genovese, 2012). The effects of these  
80 factors governing overall rheology of an emulsion gel are of considerable practical importance  
81 when utilizing an emulsion gel system for pharmaceutical, cosmetic and food applications. This  
82 article aims to provide a review about fabrication of emulsion gel systems and investigation of the  
83 main factors influencing their rheological properties.

## 84 **2. Emulsion-filled gels**

85 Emulsion-filled gels consist of oil droplets, as filler particles within a gel matrix (Torres et al.,  
86 2016). The droplets can be classified as either active or inactive fillers depending on their effect

87 on gel properties. Active fillers (so-called bound fillers) are connected to the gel network and  
88 contribute to gel strength whereas inactive (unbound) fillers show low chemical affinity to gel  
89 matrix, and do not interact or interact limitedly with gel matrix (Fig. 1) (Chen & Dickinson, 1999a;  
90 Dickinson, 2012; Oliver, Berndsen, van Aken, & Scholten, 2015). For real food emulsion gels, it  
91 is difficult to predict the precise role of filler particles because of the complex composition and  
92 unknown properties of the interfacial membranes surrounding the emulsion droplets (Chen &  
93 Dickinson, 1999a).

#### 94 *2.1. Fabrication methods*

95 Emulsion-filled gels can be produced by embedding an emulsion into either a gel phase or a pre-  
96 gel polymer solution, followed by gelation (Budai-Szucs, 2008; Dickinson, 2014). Sunflower oil  
97 emulsions stabilized by octenyl succinic anhydride-modified starch were incorporated into native  
98 starch gels to produce emulsion gels (Torres, Tena, Murray and Sarkar, 2017). In contrast,  
99 emulsions stabilized by different emulsifying agents were added into heat-denatured whey protein  
100 isolate (WPI),  $\kappa$ -carrageenan and gelatin solutions and gelation was induced by adding glucono-  
101  $\delta$ -lactone into the WPI dispersion/emulsion mixture or by cooling the carrageenan/emulsion and  
102 gelatin/emulsion mixtures (Sala, 2007). The acid-induced cold-set gelation of WPI was also  
103 employed to gelify a mixture of native WPI-stabilized emulsion and WPI aggregates (Rosa, Sala,  
104 van Vliet, and van de Velde, 2006). The embedding approach provides control over the functional  
105 performance of the whole system via the manipulation of the properties and composition of the  
106 surrounding matrix (Dickinson, 2014).

107 Emulsion-filled gels are also made through gelation of the continuous phase of an emulsion with  
108 a low or moderate oil content. Accordingly, emulsion contains a gel-able polymer in the aqueous  
109 phase (Chen & Dickinson, 1998; Kim, Renkema, & van Vliet, 2001; Lorenzo, Zaritzky, &

110 Califano, 2013; Mao, Roos, & Miao, 2014; Saxena et al., 2013). When the polymer acts as both  
111 emulsifier and gelling agent, more than enough of polymer required to completely saturate the  
112 droplet surface is added into the aqueous phase. Emulsions produced by this approach are more  
113 prone to flocculation by depletion interactions due to the present of excess unadsorbed polymer in  
114 the continuous aqueous phase of emulsion (Dickinson, 2012; Chen, Dickinson, Langton, &  
115 Hermansson, 2000). Chen and Dickinson (1998) made heat-set WPI-stabilized emulsion-filled  
116 gels by this method. They reported that the emulsion underwent extensive flocculation as a result  
117 of the use of extra whey protein during homogenization. However, as long as polymer-to-oil ratio  
118 is high enough and emulsification conditions employed are sufficiently intense, it is readily  
119 possible to create a non-flocculated emulsion with fine droplets (<1  $\mu$ m) and a narrow size  
120 distribution (Dickinson, 2012). In a study by Mao et al. (2014), cold-set emulsion-filled gels were  
121 produced through acidification of oil-in-water emulsions made by mixing WPI solution and oil,  
122 followed by high pressure homogenization using a microfluidizer. It was reported that all droplets  
123 were smaller than 300 nm, and the droplet size distribution was narrow.

124 Utilization of stimuli-responsive polymers in the formulation of emulsion gels can provide the  
125 possibility of in situ gelation. Stimuli-responsive polymers (synthetic or natural) undergo a  
126 significant physicochemical change in response to small changes in the environmental conditions  
127 which leads to a sol-gel transition in situ (Almeida, Amaral, Lobao, & Lobo, 2014; Grassi, Grassi,  
128 Lapasin, & Colombo, 2006). The stimuli capable of triggering microstructural changes include  
129 chemical (e.g., pH or ionic strength) and physical factors (e.g., temperature, magnetic fields, or  
130 mechanical stress) (Almeida et al., 2014; Gil & Hudson, 2004; Oliveira & Mano, 2015).  
131 Temperature and pH are the most widely utilized stimuli since they are easily controllable and  
132 effective in a wide range of applications (Gil & Hudson, 2004). Wan et al. (2018) produced

133 antibacterial thermo-reversible emulgels based on gelatin in order to preserve refrigerated meat.  
134 To obtain meat samples coated with the emulgels, emulsions prepared using eugenol and nonionic  
135 surfactants were added to gelatin solutions and then the pieces of meat were soaked in warm liquid  
136 emulgels. Gelation was induced during storage of the samples at 4°C (Wan et al., 2018). In a study  
137 by Soukoulis, Cambier, Hoffmann, and Bohn (2016), surfactant-stabilized o/w emulsions (5% w/w  
138 oil) containing sodium alginate and calcium carbonate were prepared. Emulsions were then mixed  
139 with glucono- $\delta$ -lactone, to trigger slow in situ release of calcium ions causing gelation of the  
140 continuous aqueous phase of emulsions. The shearing-induced gelation of inulin was exploited to  
141 cause sol-gel transition of an olive oil emulsion to filled hydrogel (Paradiso et al., 2015). Likewise,  
142 a rice bran oil and rosemary essential oil emulsion containing inulin was gelled by ultrasonic  
143 irradiation. The ultrasound was however detrimental to oil quality (Nourbehesht, Shekarchizadeh  
144 and Soltanizadeh, 2018).

145 In situ gelation of system can also be triggered by physiological stimuli such as acidic pH in the  
146 stomach (Almeida et al., 2014). Madadlou, Rakhshi and Abbaspourrad (2016) concluded that  
147 pectin and alginate-enriched milk protein-stabilized emulsions can gel in the stomach. The  
148 emulsions that gel intragastrically may be able to slow down the stomach emptying, resulting in a  
149 protracted sense of fullness. Also they can be used as carriers for the delivery of highly gastric  
150 irritant drugs, which prevent direct contact of the embedded drug with the gastric mucosa avoiding  
151 the side effects of irritant drug. In addition, these in situ gelling emulsion formulations sustain the  
152 release of the drug, which leads to better treatment efficacy and safety (de Araujo, 2014; Saxena  
153 et al., 2013). In a study by Saxena et al. (2013), in situ gelling emulsions were prepared using  
154 Gelucire 39/01 and low viscosity sodium alginate solution as lipid and aqueous phases of  
155 emulsions, respectively. Appropriate amount of CaCO<sub>3</sub> and drug were added to the prepared



156 emulsions. The authors reported formation of gel in stomach after oral administration of the  
157 emulsions and sustained release of the model drug over a period of 8 to 10 hours.

## 158 *2.2. Important factors affecting the rheology of emulsion-filled gels*

159 The rheological properties of emulsion-filled gels are different from those of conventional  
160 hydrogels with the same nature of the gel matrix and depend on several factors such as  
161 characteristics of filler and matrix and also interactions between them (Dickinson & Yamamoto,  
162 1996b; Genovese, 2012; McClements, Monahan, & Kinsella, 1993; Torres et al., 2016). Some of  
163 the most important of these factors are described below.

### 164 *2.2.1. Type and concentration of emulsifying agent*

165 The type of emulsifier adsorbed to the surface of droplets dictates the nature of interactions  
166 between droplet and gel network (Torres et al., 2016). Active fillers enhance or diminish emulsion  
167 gel modulus depending on the ratio between droplet modulus and that of the gel matrix (Chen &  
168 Dickinson, 1999b; Oliver, Scholten, & van Aken, 2015). For an emulsion droplet, shear modulus  
169 is related to the Laplace pressure (Equation 1), which is proportional to the ratio of interfacial  
170 tension ( $\gamma$ ) to droplet radius R (Chen & Dickinson, 1999a; Walstra, 2003).

$$171 \quad G' = p_L = 2\gamma/R \quad (\text{Eq. 1})$$

172 The enhancement of emulsion gel modulus ( $G'$ ) occurs when the droplet modulus is higher than  
173 the modulus of gel matrix (Chen & Dickinson, 1999a; Sala, 2007). On the other hand, inactive or  
174 non-interacting fillers in the network are expected to behave like small holes in a composite  
175 material (Dickinson, 2012). Therefore, they may weaken the gel and disrupt the network. In heat-  
176 set emulsion gels that whey protein served as the sole emulsifier and gelling agent, the protein-  
177 covered oil droplets behaved as active filler particles conferring a high viscoelasticity to gel;

178 however, in the presence of an excess amount of a non-ionic surfactant, droplets behaved as  
179 inactive fillers and the gel texture weakened (Chen et al, 2001).

180 In emulsion systems containing a mixture of polymer and surfactant, rheological character  
181 becomes more complex because they both contribute to emulsion stability and rheological  
182 properties. Rheological properties of such emulsion gel systems can be affected by polymer-  
183 surfactant interactions and their effects on polymer adsorption at interface and chemical affinity  
184 between filler and matrix. In the case of proteins, unfolding and aggregation of protein molecules  
185 can also be affected by surfactants, which influence the rheological behavior of protein-based  
186 emulsion gels containing surfactant. The effects of polymer-surfactant interactions depend on the  
187 type of added surfactant (non-ionic, cationic or anionic), concentration of surfactant and the  
188 solution conditions such as pH, temperature and ionic strength (Dickinson & Hong, 1997).

189 Surfactants can influence adsorption of polymers at interface through two different mechanisms  
190 including binding of surfactant to the polymer, which alters polymer solubility, and the competitive  
191 adsorption between the adsorbed polymer and surfactant (Guzman et al., 2016; Kronberg,  
192 Holmberg, & Lindman, 2014). If there is a strong attraction between the surfactant and the  
193 polymer, adsorption of the polymer can be enhanced as a result of decreased solvency. This can  
194 be explained by the fact that association of an ionic surfactant to oppositely charged polymer  
195 reduces the polymer charge, which leads to compaction of the polymer chain and a diminished  
196 solubility. Thereby, an enhanced adsorption of the surfactant–polymer complex can be attained  
197 due to charge neutralization (Chen & Dickinson, 1995a; Chen & Dickinson, 1995b; Kronberg et  
198 al., 2014). At higher surfactant concentrations, the surfactant–polymer complex achieves the same  
199 charge as the surfactant and becomes soluble because of its high charge density. In this region of  
200 surfactant concentration, the polymer–surfactant complexes do not adsorb and the interface is

201 covered with adsorbed surfactant only (Chen & Dickinson, 1995b; Kronberg et al., 2014). As well,  
202 if an ionic surfactant is added to a non-charged polymer pre-adsorbed onto interface, the polymer  
203 desorbs from the surface due to binding of the surfactant to the polymer via hydrophobic  
204 interactions, and forming a soluble polymer–surfactant complex with the charges originating from  
205 the surfactant (Kronberg et al., 2014).

206 In addition to the mechanism of formation of soluble complexes causing polymer desorption,  
207 polymers can also be desorbed from an O/W interface due to competitive adsorption between the  
208 adsorbed polymer and surfactant (Chen & Dickinson 1995c; Guzman et al., 2016). When there is  
209 a repulsive interaction or a weak attractive interaction between the surfactant and the polymer, i.e.  
210 the surfactant and polymer have the same charge or surfactant is non-ionic, then the surfactant can  
211 displace the polymer from the interface to reduce the surface energy (Guzman et al., 2016;  
212 Kronberg et al., 2014). Under such conditions and at below the critical micelle concentration  
213 (CMC) of the surfactant, both the polymer and the surfactant are adsorbed to interface. Above the  
214 CMC, almost all polymer is desorbed and only the surfactant is present at the interface (Kronberg  
215 et al., 2014).

216 In the case of protein-surfactant mixed systems, some different behavior may be seen due to the  
217 specific secondary and tertiary structures of proteins (Guzman et al., 2016). In particular, globular  
218 proteins as the most frequently studied proteins are different from the other polymers since they  
219 are compact and monodisperse macromolecules with lack of conformational freedom (Piculell,  
220 Lindman, & Karlstrom, 1998). Proteins can interact with surfactants with both hydrophobic and  
221 electrostatic interactions due to their amphiphilic character and net charge (Kronberg et al., 2014).  
222 Binding of larger amounts of surfactant to a protein, especially for ionic surfactants, may lead to a  
223 drastic conformational change that is irreversible and can give rise to the complete denaturation of

224 the protein. Therefore, proteins may be involved in different conformational states which  
225 complicates studies of interactions (Piculell et al., 1998). It is established that surfactants can be  
226 classified into two categories: denaturing surfactants which complex to proteins and induce  
227 unfolding of their tertiary structure, and non-denaturing surfactants in which the tertiary structure  
228 is maintained (Jones & Brass, 1991). Nonionic surfactants such as the Tritons or n-octyl- $\beta$ -  
229 glucoside (OBG), have minor effects on the tertiary structure of proteins. On the other hand, ionic  
230 surfactants tend to associate strongly with proteins and can then initiate unfolding of their tertiary  
231 structure. Anionic surfactants, e.g. sodium n-dodecylsulphate (SDS), can unfold proteins more  
232 than cationics (Jones & Brass, 1991). One of interesting manifestations of the amphiphilic nature  
233 of proteins is when a surfactant is added to a concentrated solution of a protein. Surfactant addition  
234 leads to a considerable enhancement in viscosity with a maximum as a function of the surfactant  
235 concentration (Kronberg et al., 2014). This viscosity effect is attributed to the formation of mixed  
236 micelle-like aggregates containing surfactants and hydrophobic groups belonging to two distinct  
237 protein chains. The mixed micelles cross-link the protein molecules (Dickinson & Hong, 1997;  
238 Djabourov, Nishinari, & Ross-Murphy, 2013). This behavior has similarities with that suggested  
239 for systems containing mixtures of hydrophobically modified water-soluble polymers and  
240 surfactants. At higher surfactant concentrations, the cross-linking effects are eliminated because  
241 each of the mixed micelles will contain only one hydrophobic group (Fig. 2). It has been shown  
242 that anionic surfactants, at concentrations above the CMC, are more effective in increasing the  
243 viscosity of gelatin solutions than cationic surfactants. As well, nonionic surfactants have  
244 negligible effect on the gelatin solution viscosity (Chen & Dickinson, 1995b).

245 Dickinson and Hong (1997) studied the influence of sodium dodecyl sulphate (SDS), as an anionic  
246 surfactant, on the rheology of heat-set  $\beta$ -lactoglobulin-stabilized emulsion gels. They found that

247 the storage modulus of emulsion gel was highly dependent on the total protein content and,  
248 specifically, the surfactant/protein molar ratio. For low surfactant additions to the concentrated  
249 emulsion systems, the storage modulus tended slightly to decrease as a consequence of increased  
250 electrostatic repulsion between the droplets caused by surfactant binding (Dickinson & Hong,  
251 1997). At intermediate SDS concentrations, the storage modulus increased which was attributed  
252 to SDS-induced unfolding of protein and surfactant-mediated cross-links via mixed micellar  
253 aggregates (Dickinson & Hong, 1997). The authors also reported that a large reduction in the  
254 storage modulus at high surfactant/protein molar ratio in the concentrated emulsions was due to  
255 complete solubilization of protein into discrete unconnected mixed micelles. In systems containing  
256 an anionic water-dispersible emulsifier diacetyl tartaric acid ester of monoglyceride (DATEM), it  
257 was found that the storage modulus of emulsion gel increased with increasing surfactant/protein  
258 molar ratio due to poor ability of DATEM to displace the adsorbed protein competitively  
259 (Dickinson, 2012; Dickinson and Hong, 1994; Dickinson & Hong, 1997).

260 For nonionic emulsifier in mixed surfactant-protein systems, it has been shown that replacement  
261 is the predominant mechanism (Dickinson & Hong, 1995; Guzman et al., 2016). Non-ionic water-  
262 soluble surfactants such as Tween 20 are more effective in displacing proteins from oil-water  
263 interfaces compared to oil-soluble emulsifiers e.g., glycerol monostearate (Dickinson, 2012). For  
264 a protein-stabilized emulsion gel, as the proteins start to displace from the droplet surface in the  
265 presence of Tween 20, chemical affinity between the filler and the matrix is weakened which leads  
266 to a decrease in the storage modulus of emulsion gel (Torres et al., 2016).

### 267 2.2.2. Filler concentration and size

268 The influence of filler concentration on the rheology of emulsion-filled gels depends on the type  
269 of filler (Dickinson & Chen, 1999). It has been reported by several authors that gel strength

270 increases with increasing filler concentration for droplets bound to matrix, i.e. active droplets  
271 (Boutin, Giroux, Paquin, & Britten, 2007; Gwartney, Larick, & Foegeding, 2004; Line,  
272 Remondetto, and Subirade, 2005; Rosa et al., 2006). Sala (2007) found that the fracture strain  
273 decreased with increasing oil concentration for droplets interacted to the matrix such as gelatin  
274 gels with WPI-stabilized emulsions and WPI gels with WPI aggregate-stabilized emulsions,  
275 whereas remained constant for noninteracting droplets including gelatin gels with Tween-  
276 stabilized emulsions and k-carrageenan gels with WPI-stabilized emulsions. van Vliet (1988)  
277 studied dynamic moduli of casein gels and polyvinyl alcohol (PVA)-Congo red gels filled with  
278 particles as a function of filler type and volume fraction of fillers. He showed that if there was no  
279 interaction between the fillers and gel matrix, the modulus decreased with increasing volume  
280 fraction of the filler for both the filled PVA and the filled casein gels.

281 Droplet volume fraction can be influenced by distribution of the droplets in the gel matrix (Oliver  
282 et al., 2015). Flocculated state of droplets within the gel matrix causes a higher effective volume  
283 fraction of filler as compared with single droplets due to the matrix entrapped within the  
284 flocculated droplets. For an emulsion gel system with bound and flocculated droplets, a higher  
285 effective volume fraction results in greater values of viscoelastic parameters (Chen & Dickinson,  
286 1998; Sala, 2007). van Vliet (1988) reported that the increase in elastic moduli, as a function of  
287 the volume fraction of fillers, for casein gels containing active fillers (milk fat globules) was much  
288 greater than expected. He explained that during the gel formation process, the milk fat globules  
289 became flocculated. Since the volume of such a flocculated particle composed of fat globules was  
290 greater than the sum of the volumes of individual globules, the effective volume fraction of  
291 dispersed fat globules was enhanced which led to a higher elastic moduli of the filled casein gels.  
292 Similar trends of effect of the increased effective volume fraction of dispersed phase on elastic

293 modulus of gels, induced by droplet flocculation, have been reported for heat-set whey protein  
294 emulsion gel systems (Chen & Dickinson, 1998) and soy protein emulsion gel systems (Kim et al.,  
295 2001).

296 In terms of filler size, smaller average particle sizes tend to enhance the filler effect due to an  
297 increase in surface area-to-volume ratio and in the number of filler particles which reduces distance  
298 between droplets (Dickinson & Chen, 1999; Torres et al., 2016). Several studies conducted on  
299 large deformation and fracture properties of emulsion gels have indicated that, at a constant volume  
300 fraction, gel strength increases as the size of active fillers decreases. For example, in the case of  
301 soybean protein isolate gels containing oil droplets stabilized by soy protein and WPI gels  
302 containing emulsions stabilized by WPI, as well myofibrillar protein (MP) gels containing MP-  
303 coated oil droplets, lowering of the oil droplet size resulted in a higher gel strength for gels (Kim  
304 et al., 2001; Yost & Kinsella, 1993; Wu, Xiong, & Chen, 2011). On the other hand, for gels  
305 containing emulsions stabilized by SDS, Tween 20 and Triton X-100, i.e. inactive filler particles,  
306 no effect of the droplet size on gel strength was observed (McClements et al., 1993). Sala (2007)  
307 found that the effect of a decrease in the size of oil droplet on the Young's modulus of gels with  
308 non-flocculated bound droplets and that of gels with droplets unbound to the matrix was according  
309 to the van der Poel theory, unless when the droplets were flocculated.

310 Van der Poel theory can predict the shear modulus of filled gels for a given moduli of gel matrix  
311 ( $G'_{\text{matrix}}$ ) and filler particles ( $G'_{\text{filler}}$ ), provided that the filler particles are assumed to behave as  
312 bound fillers, and also be non-interacting with each other (Geremias-Andrade et al., 2016). The  
313 theory expresses when the filler particles are more rigid than the gel matrix ( $G_{\text{filler}} > G_{\text{matrix}}$ ), the  
314 shear modulus of the filled gel is higher than that of the matrix, whereas a reversed trend is  
315 predicted for the situation of  $G_{\text{filler}} < G_{\text{matrix}}$  (Geremias-Andrade et al., 2016; Sala, 2007). To

316 calculate the modulus of gels containing unbound fillers, a modification of the van der Poel theory  
317 was proposed by [van Vliet \(1988\)](#) via setting the filler modulus to zero. On the basis of this theory,  
318 [Sala \(2007\)](#) demonstrated that for gels with non-flocculated bound fillers, e.g. gelatin gels  
319 containing emulsions stabilized by WPI, a decrease of the filler size **caused** stiffening of the fillers  
320 and, therefore, results in an increase of the Young's modulus of filled gels. In the case of unbound  
321 droplets (k-carrageenan gels with WPI-stabilized emulsions and gelatin gels with Tween-stabilized  
322 emulsions), he reported that droplet size alterations exerted no effect on the Young's modulus of  
323 gels which corroborates the approximation of setting the effective modulus of unbound droplets to  
324 zero ([Sala, 2007](#)). In gel systems containing flocculated bound droplets, if the flocs modulus is  
325 greater than the modulus of the gel matrix, larger flocs can induce an enhanced effective volume  
326 of the fillers, resulting in an increase of the filled gel modulus, whereas the opposite trend may  
327 occur for gels containing the flocs with a lower modulus than that of the matrix ([Sala, 2007](#)).

### 328 2.2.3. Solid fat content

329 Replacement of a liquid oil by a solid fat in an emulsion leads to an increased stiffness of the  
330 emulsion-filled gel ([Oliver et al., 2015](#)). The modulus of droplets with solid fat content is enhanced  
331 by the presence of a fat crystal network which is formed due to aggregation of crystals via van der  
332 Waals attraction ([Kloek, van Vliet, & Walstra, 1997](#); [Torres et al., 2016](#)). [Oliver et al., \(2015\)](#)  
333 investigated alteration in rheological behaviour of emulsion-filled gels when a high saturated solid  
334 fat is replaced by unsaturated liquid oil. They demonstrated that the hardness of the fat phase  
335 formed inside the emulsion droplets increases the modulus of the emulsion gel. Therefore, gels  
336 comprising droplets with a higher solid fat content possess larger modulus values than those  
337 containing droplets of liquid oil ([Oliver et al., 2015](#)). Furthermore, partial coalescence phenomena  
338 can occur when fat crystals located near the interface protrude into the aqueous phase, pierce the



339 film separating two droplets and penetrate into the oil phase of adjacent droplets. This causes the  
340 droplets to stay flocculated (Leal-Calderon et al., 2007; McClements, 2015). As a consequence,  
341 the effective volume fraction of droplet increases, which can stiffen the emulsion gel (Torres et  
342 al., 2016).

#### 343 2.2.4. Matrix stiffness

344 As mentioned earlier, the modulus of gel matrix influences rheological properties of the emulsion-  
345 filled gel. Elastic modulus of the gel matrix is significantly affected by polymer concentration  
346 (Geremias-Andrade et al., 2016). In a study on the rheological properties of emulsion-filled protein  
347 gels, Mao et al. (2014) reported that gels with a higher protein content had a higher storage  
348 modulus and showed a higher force and strain at breaking, which was attributed to formation of a  
349 more compact gel network. Soltani and Madadlou (2016) demonstrated that pectin gels containing  
350 Pickering emulsions became harder with increasing pectin content. They also reported that gelation  
351 time was shorter at a higher content of pectin. Increasing the gelling agent concentration causes  
352 polymer chains to come closer together, resulting in a reduction in the number of voids in the  
353 matrix and formation of more bonds between structural elements. This increases the elastic  
354 modulus of gel matrix (Oliver et al., 2015; Torres et al., 2016). The type of polymer utilized as  
355 gelling agent can influence matrix stiffness. In a study by Lorenzo et al. (2013), two types of gellan  
356 (high and low-acyl versions) were used as gelling agent to produce emulsion-filled gels. The  
357 authors reported that only high acyl gellan formed stable emulsion gels. The emulsion gels  
358 formulated by low acyl gellan remained fluid for a longer time, which allowed oil droplets to  
359 cream. Emulsion-filled gels based on high acyl gellan gum exhibited a “strong gel-like” behavior  
360 with a frequency-independent storage modulus (Lorenzo et al., 2011).

#### 361 2.4.5. Interfacial ageing

362 Age of the interfacial layer of biopolymers influences the extent of the reinforcing effect of the  
363 fillers (Dickinson, 2012). Chen and Dickinson (1999b) studied the interfacial ageing effect of  
364 protein monolayer around the droplets on the viscoelasticity of a heat-set protein emulsion gel. In  
365 this study  $\beta$ -lactoglobulin-stabilized emulsions were made and then either mixed immediately with  
366 whey protein isolate or left for up to few days before mixing and thermal processing. They found  
367 that the aged monolayer had weaker chemical affinity for the gel matrix leading to less influence  
368 on increasing the viscoelasticity of the final gel. The loss of interfacial reactivity was attributed to  
369 rapid conformational changes in the adsorbed protein structure, leading to formation of lateral  
370 intra-layer cross-links between adsorbed protein molecules and correspondingly a reduction in  
371 cross-links between the adsorbed proteins and the proteins of the gel matrix (Chen, & Dickinson  
372 1999b; Dickinson, 2012; Torres et al., 2016).

### 373 *2.3. Water-holding capacity*

374 Water-holding capacity of emulsion-filled gels is related to their microstructural properties (Line  
375 et al., 2005). Two different types of microstructure can be distinguished for the gel matrix of  
376 emulsion-filled gels: particulate and fine-stranded gel matrixes (Fig. 3) (Gwartney et al, 2004).  
377 Particulate gel matrixes consist of a three-dimensional network of rather large aggregates  
378 composed of numerous biopolymer molecules. These highly aggregated gels possess coarser  
379 network structures with large pores between the polymeric aggregates, which makes them prone  
380 to syneresis because it is not possible to hold water tightly by capillary forces (McClements, 2015).  
381 Particulate gels of globular proteins are formed at pH values close to the iso-electric point of  
382 protein or at high salt concentrations (Nicolai & Durand, 2013). In fine-stranded gels, biopolymer  
383 molecules build up thin filaments and have a low tendency to aggregate further (Hermansson,  
384 2008). For these finer gel matrixes, smaller and more homogenous pore sizes mean that the water

385 are held tightly by capillary forces and cannot be pressed out (Bryant & McClements, 1998;  
386 Hermansson, 2008). Gels formed by a large number of hydrocolloids such as pectin, agar, gelatin,  
387 gellan, alginate, etc. have fine-stranded structure. In the case of globular proteins, fine stranded  
388 gels are formed at low ionic strengths and pH values significantly far from the isoelectric point of  
389 protein (Nicolai & Durand, 2013). Under these conditions, protein molecules do not undergo  
390 extensive aggregation owing to the strong electrostatic repulsion between them (Bryant &  
391 McClements, 1998). A number of factors can influence the matrix microstructure of emulsion gels  
392 such as oil concentration, polymer concentration, ionic strength and thermal treatment (Line et al.,  
393 2005; Mao et al., 2014). Increasing the concentration of oil droplets acting as bound fillers  
394 decreases emulsion gel syneresis. Bound fillers, as an integrated part of the gel matrix, diminish  
395 the effective pore size of gel network and obstruct micro-channels, thereby leading to a reduction  
396 in water release when pressure is applied to the gel (Boutin et al., 2007; Line et al., 2005).

397 Emulsion gels with a higher polymer content have a higher water-holding capacity due to  
398 formation of a more compact gel network with lower permeability. Boutin et al. (2007) reported  
399 that the syneresis of WPI emulsion gels was significantly affected by whey protein concentration.  
400 The effect of polymer content on syneresis of emulsion-filled gels is more pronounced than that  
401 of oil, which is probably due to the water-binding sites that exist on biopolymer chains (Mao et  
402 al., 2014).

403 Gel structure and water-holding capacity can be affected by calcium ion level. A mixture of Na<sup>+</sup>  
404 (25 mM NaCl) and Ca<sup>2+</sup> (10 mM CaCl<sub>2</sub>) caused formation of particulate heat-set WPI emulsion  
405 gels at pH 7.0 in comparison to Na<sup>+</sup> (25 mM NaCl) that produced stranded gels (Gwartney et al.,  
406 2004). The particulate emulsion gel held less water than the stranded gel. Similarly, Line et al.  
407 (2005) observed that an increase in Ca<sup>2+</sup> level from 11.7 to 68.3 mM changed the cold-set β-

408 lactoglobulin emulsion gel microstructure from fine-stranded, with small pore size, to particulate  
409 microstructure comprising larger protein aggregates and larger pores. Gel microstructure is also  
410 affected by thermal treatment before or after emulsification. The water holding capacity of cold-  
411 set soy protein isolate (SPI) emulsion gels induced by CaCl<sub>2</sub> and glucono- $\delta$ -lactone was enhanced  
412 by thermal treatment after emulsification, whereas thermal treatment before emulsification led to  
413 a slight decrease in water-holding capacity. Thus, formation of protein aggregates before  
414 emulsification was not in favor of gel microstructure, whereas thermal treatment after  
415 emulsification leading to unfolding and aggregation of proteins adsorbed at the oil-water interface  
416 improved the microstructural properties of emulsion gels. The improvement was a consequence of  
417 enhanced inter-droplet interactions and interactions between adsorbed and unadsorbed proteins  
418 (Tang, Chen, and Foegeding, 2011). Heat treatment duration and temperature is significant  
419 because they influence protein aggregation extent (Torres et al. 2016). A stronger thermal  
420 treatment causes a more significant denaturation and more exposure of hydrophobic domains,  
421 thereby leading to extensive aggregation of protein molecules (Ruffin, Schmit, Lafitte, Dollat, &  
422 Chambin, 2014).

### 423 **3. Emulsion particulate gels**

424 Controlled clustering of droplets can be utilized to produce emulsion gel systems with particle gel  
425 microstructures (Bremer, Bijsterbosch, Walstra, & Van Vliet, 1993; Dickinson, 2012). A particle  
426 gel consists of a collection of aggregated particles, which occupy the enclosing volume, forming  
427 a continuous three-dimensional network (Fig. 4) (Bremer, 1992; Sala, 2007). It is noteworthy that  
428 some authors use the terms aggregation and flocculation interchangeably, whereas others  
429 distinguish between the two terms. Nonetheless, the distinction has not a significant practical  
430 importance (Dickinson, 2010). Here, the term ‘flocculation’ may be replaced by ‘aggregation’

431 without significant loss of meaning. Rheology of a particle gel can be mainly affected by strength  
432 of interaction forces between the particles and also deformability of the particles (Bremer, 1992;  
433 Walstra, 2003). In the case of oil droplets, deformability is determined by the Laplace pressure  
434 within the droplet (Oliver et al., 2015). It has been reported that when particles are less deformable  
435 and the strands of aggregated particles are less flexible and curved, it will result in smaller fracture  
436 strains for emulsion gels (van Vliet, 2013).

437 Based on the nature of the interactions between the droplets, aggregation and gelation of emulsion  
438 droplets may be strong and irreversible or weak and reversible (Dickinson, 2010; Petsev, 2002,  
439 2004).

### 440 *3.1. Irreversible aggregation*

441 In irreversible aggregation and gelation, droplets stick together very strongly and form permanent  
442 fractal-type flocs (Dickinson, 2000; Genovese, 2012). These flocs grow large enough to join  
443 together and ultimately form large interconnected macroscopic networks (Blijdenstein, Hendriks,  
444 van der Linden, van Vliet, & van Aken, 2003; Dickinson, 2000). The resulting structure of the  
445 flocs is related to aggregation mechanisms and the interparticle interactions (Tirado-Miranda,  
446 Rodríguez-Valverde, Schmitt, Callejas-Fernández, & Fernandez-Barbero, 2009). Two idealized  
447 mechanisms of particle aggregation considered for irreversible processes are diffusion-limited  
448 cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA) (Bremer et al., 1993;  
449 Dickinson, 2000; Djabourov et al., 2013). In the case of DLCA model, repulsive forces are  
450 negligible and every collision between particles or clusters leads to irreversibly attachment upon  
451 contact (Bremer, 1992; Turgeon & Laneuville, 2009). Such a fast aggregation process results in  
452 more open and porous flocs of lower fractal dimension because of little time for rearrangement of  
453 the flocs (Bremer, 1992; Grassi et al., 2006). In the RLCA model, particles still possess a small

454 but nonnegligible repulsive barrier that must be overcome before the particles irreversibly join  
455 together (Del Gado et al., 2016). Since particles do not immediately stick and the aggregation rate  
456 is slower, the particles can diffuse further within a growing aggregate which results in more  
457 interpenetrated and compact flocs with higher fractal dimension (Bremer, 1992; Del Gado et al.,  
458 2016; Grassi et al., 2006). In a polymer-stabilized emulsion, when approximately all the available  
459 gelling polymer is located at the interface and only a trace amount of excess polymer exists in the  
460 continuous aqueous phase, flocculation and gelation can occur through direct links between  
461 polymers located at different droplet surfaces (Chen & Dickinson, 1999b). As a consequence, a  
462 particle gel with polymer-coated emulsion droplets comprising the primary structural units is  
463 formed. Some of the most common physico-chemical processes used to induce irreversible  
464 flocculation and gelation of polymer-coated droplets are explained below.

#### 465 3.1.1. Altering pH and ionic strength

466 For electrostatically stabilized emulsions fabricated by using electrically charged emulsifiers, e.g.,  
467 ionic surfactants, proteins, or polysaccharides, flocculation can be induced by changing pH and  
468 ionic strength of the surrounding aqueous phase or by binding divalent ions especially  $\text{Ca}^{2+}$  to  
469 adsorbed emulsifier molecules (Dickinson, 2010; McClements, 2015). In protein-stabilized  
470 emulsions, the net charge on the protein is relatively low upon approaching the isoelectric point  
471 and the electrostatic repulsion forces between the droplets are no longer sufficiently strong to  
472 prevent droplets from getting close together, leading to flocculation. Chen, Dickinson and Edwards  
473 (1999) and also Chen and Dickinson (2000) produced sodium caseinate emulsion gels through  
474 acidification of sodium caseinate stabilized emulsions by adding glucono- $\delta$ -lactone. Large  
475 deformation behavior of the produced emulsion gels was more like a typical particle gel which  
476 includes short linear viscoelastic region and shear-weakening behavior beyond the linear region

477 (Chen & Dickinson, 1999b, 2000; Chen et al., 1999). An increase in ionic strength of the  
478 surrounding solution under influence of concentration and valence of the ions leads to a  
479 progressive screening of the electrostatic repulsion between droplets, which results in flocculation  
480 (McClements, 2015). Tang and Liu (2013) prepared gel-like soy protein emulsions by means of  
481 microfluidization at appropriate NaCl concentrations. They demonstrated that attractive inter-  
482 droplet interactions and subsequently, the extent of droplet flocculation increased due to  
483 electrostatic repulsion screening of charged groups of the adsorbed proteins by the salt. The  
484 minimum amount of electrolyte required to induce flocculation, defined as critical flocculation  
485 concentration (CFC), decreases with increasing the valence of the counter ions and decreasing the  
486 surface potential of droplets (Tadros, 2006).

487 Monovalent counter-ions screen electrostatic interactions but do not change the surface charge  
488 density or isoelectric point of charged emulsion droplets; whereas, multivalent counter-ions, in  
489 addition to being more effective in charge screening, alter the surface charge density and isoelectric  
490 point of emulsion droplets by binding to the surface of droplets (Guzey & McClements, 2006;  
491 McClements, 2015). Thereby multivalent counter-ions are particularly efficient at lowering  
492 flocculation stability of the electrostatically stabilized emulsions than monovalent counter-ions  
493 (McClements, 2004).

### 494 3.1.2. Thermal processing

495 In the case of emulsions stabilized by globular proteins, hydrophobic interactions play a significant  
496 role in determining the flocculation stability (McClements, 2015). It has been shown that surface  
497 denaturation at relatively low temperatures (below 65°C) and unfolding at thermal denaturation  
498 temperature of adsorbed globular proteins after emulsification can cause exposure of hydrophobic  
499 segments, which leads to flocculation of emulsion droplets by thermal treatment or ageing,

500 depending on the content of non-adsorbed protein and ionic strength (Dickinson, 2010). Dickinson  
501 and Chen (1999) produced heat-set whey protein-stabilized emulsion gels behaving more like  
502 particle gels at oil volume fractions more than 30 %.

### 503 3.1.3. Bridging flocculation

504 Formation of bridges between polymers either during emulsification or after it can result in  
505 emulsion droplets flocculation (Dickinson, 2010). Bridging flocculation during emulsification  
506 occurs when concentration of a polymer used as emulsifier is insufficient to completely cover the  
507 interface and hence the same polymer adsorbs simultaneously onto more than one droplet. This  
508 leads to formation of “bridges” or “links” between oil droplets (Kronberg et al., 2014; Pal, 1996).  
509 After emulsification, bridging flocculation and gelation can be induced by mixing an emulsion  
510 containing electrically charged polymer-coated droplets with a solution of oppositely charged  
511 polymers at a concentration below that required for total surface coverage (Dickinson &  
512 Pawlowsky, 1997). Simo, Mao, Tokle, Decker, and McClements (2012) prepared emulsion-based  
513 gel systems by addition of pectin solution to emulsions containing  $\beta$ -lactoglobulin-coated lipid  
514 droplets at pH values lower than the isoelectric point of  $\beta$ -lactoglobulin ( $pI \approx 5$ ) where the droplets  
515 were positively charged and the pectin molecules were negatively charged. Consequently, pectin  
516 molecules were attracted to the surfaces of protein-coated droplets leading to droplet aggregation  
517 and gel formation by a bridging flocculation mechanism (Simo et al., 2012). If the protein-coated  
518 droplets are fully covered by added anionic polymers, then bridging flocculation is replaced by a  
519 restabilization mechanism arising from the electrostatic and steric repulsion between the droplets  
520 (Dickinson & Pawlowsky, 1997).

### 521 3.1.4. Enzyme treatment



522 The enzyme transglutaminase (glutaminyl-peptide  $\gamma$ -glutamyltransferase, EC 2.3.2.13) can  
523 covalently cross-link most proteins through the formation of  $\epsilon$ -( $\gamma$ -glutamyl)lysine bridges  
524 (Matsumura, Kang, Sakamoto, Motoki, & Mori, 1993; Zeeb, Fischer, & Weiss, 2014). Flexible  
525 proteins such as gelatin and casein are good substrates for this enzyme, while globular proteins, in  
526 native state, are poor substrates owing to their compact structure which limits the accessibility of  
527 enzyme to the target glutamine and lysine residues (Lim, Mine, Britt, & Tung, 2002).

528 Aggregation of droplets in a protein-stabilized oil-in-water emulsion is conveniently achieved  
529 using transglutaminase treatment through crosslinking between protein molecules adsorbed on  
530 different droplets (Chanyongvorakul, Matsumura, Sawa, Nio, & Mori, 1997). In systems of high  
531 volume fraction with sufficiently extensive crosslinking, the liquid-like emulsion will be converted  
532 into an emulsion gel (Dickinson, 1997). Dickinson and Yamamoto (1996a) produced  
533 transglutaminase-induced milk protein gels and emulsion gels and as well, compared rheological  
534 properties of these systems with those of the equivalent heat-induced gels and emulsion gels. They  
535 found that, for protein gels (no oil droplets) the enzymatic treatment made a stronger gel than the  
536 heat processing while for the emulsion gels, the opposite trend was observed. The authors  
537 explained that these differences in rheological behavior was due to the presence of unbreakable  
538 crosslinks in the enzyme-treated system imposing topological constraints, which prevents some  
539 adsorbed protein molecules from making crosslinks with other adsorbed protein molecules and  
540 limits further strengthening of the network via subsequent structural rearrangements in the  
541 emulsion gel (Dickinson & Yamamoto, 1996a).

#### 542 3.1.5. High-pressure processing

543 Flocculation and gelation of concentrated emulsions stabilized by globular proteins can be induced  
544 by the application of high pressure (Dickinson & James, 1998). As with thermal treatment, pressure

545 processing can denature globular proteins and lead to aggregation (Galazka, Dickinson, &  
546 Ledward, 2000). The effect of pressure on proteins is rather complex and depends on the protein  
547 structure, pH, ionic strength, solvent composition and pressure processing conditions such as  
548 temperature, the magnitude and duration of the applied pressure (Dumay, Kalichevsky, & Cheftel,  
549 1994; Galazka et al., 2000). It has been found that intramolecular hydrophobic and electrostatic  
550 interactions are affected by pressure but hydrogen bonds are virtually insensitive to the applied  
551 pressure (Galazka et al., 2000; Messens, Van Camp, & Huyghebaert, 1997). This means that the  
552 tertiary and quaternary structure of globular proteins are disrupted while their secondary structure  
553 is relatively unaffected (Singh & Ye, 2014).

554 Dickinson and James (1998) produced  $\beta$ -lactoglobulin-stabilized emulsion gels through  
555 application of high pressure and thermal treatment. They reported that maximum values of elastic  
556 moduli for emulsion gels fabricated by thermal treatment ( $T_{\max} = 80\text{ }^{\circ}\text{C}$ ) can be some 2-3 orders  
557 of magnitude higher than for those fabricated by high-pressure treatment ( $P_{\max} = 800\text{ MPa}$ ). It was  
558 found that the emulsion gel made by severe high-pressure processing (800 MPa for 60 min) can  
559 possess viscoelastic properties that are almost the same as those for the equivalent emulsion gel  
560 made by mild thermal treatment (65°C for 5 min). Therefore, high-pressure processing can be  
561 considered as a milder treatment in comparison with thermal treatment (Dickinson, 2012;  
562 Dickinson & James, 1998).

### 563 3.2. Reversible aggregation

564 In reversible aggregation and gelation, emulsion droplets stick together by moderately weak forces  
565 to form a transient network possessing viscoelastic properties of a weak gel-like solid (Dickinson,  
566 2000; Genovese, 2012). It was found that in systems containing high concentrations of oil and  
567 polymer, a weak and reversible particle gel network can be formed by the mechanism of depletion

568 flocculation even without further processing (Dickinson, 2012; Dickinson & Golding, 1997).  
569 Depletion flocculation tends to occur when there is excess unadsorbed colloidal particles, such as  
570 polymer molecules or surfactant micelles in the continuous phase (Dickinson, 2012; McClements,  
571 2009). In such systems, as two droplets approach each other, there will be a point where there is  
572 no longer space for unadsorbed colloidal particles between the droplets (Kronberg et al., 2014).  
573 The exclusion of the colloidal particles from this narrow region between two droplets gives rise to  
574 an osmotic pressure gradient driving solvent molecules out of this area into the bulk liquid in order  
575 to dilute the surrounding colloid-rich solution. These entropic exclusion and osmotic effect result  
576 in a net attraction between the droplets causing flocculation (Appelqvist, Golding, Vreeker, &  
577 Zuidam 2016; McClements, 2000). Dickinson and Golding (1997) investigated the influence of  
578 unadsorbed protein on the stability of emulsions prepared with sodium caseinate. They  
579 demonstrated that in emulsions containing relatively high concentrations of both protein and oil, a  
580 weak particle gel network was formed by depletion flocculation of oil droplets due to caseinates  
581 remaining unadsorbed and forming sub-micelles in the aqueous phase. In a study on formation of  
582 emulsion-based gel-like materials, Simo et al., (2012) showed that mixing an emulsion containing  
583  $\beta$ -lactoglobulin-coated lipid droplets with a pectin solution under conditions where the droplets  
584 and pectin molecules had similar charges (i.e., at pH 7) can induce depletion flocculation and gel  
585 network formation above a critical pectin concentration. It was ascribed to the presence of pectin  
586 molecules, which are not attracted to the droplet surfaces.

### 587 *3.3. Heteroaggregation*

588 In contrast to aggregation of similar colloidal particles (homoaggregation) in single-particle  
589 systems, heteroaggregation phenomenon can occur between particles of different types in mixed  
590 particle systems (Dickinson, 2011; Lopez-Lopez, Schmitt, Moncho-Jorda, & Hidalgo-Alvarez,

591 2006). For a binary emulsion system, in which each emulsion separately is stabilized  
592 electrosterically by biopolymers having different isoelectric points, heteroaggregation of  
593 oppositely charged droplets and also gelation of system may occur under certain conditions  
594 (Dickinson, 2011). In dilute mixed systems, discrete clusters of charged droplets with various sizes  
595 and structures are formed depending on the nature and ratio of the positive and negative droplets  
596 involved (Dickinson, 2011; Mao & McClements, 2011, 2012a). In concentrated systems, created  
597 clusters extend all over the volume of the system which lead to the formation of particle gel  
598 network (Dickinson, 2011; Mao & McClements, 2011). Mao and McClements (2011) prepared  
599 gel-like mixed-protein emulsions based on heteroaggregation, through mixing an emulsion  
600 stabilized by  $\beta$ -lactoglobulin with another emulsion stabilized by lactoferrin. These two proteins  
601 possess different isoelectric points ( $\beta$ -lactoglobulin  $pI \approx 5$  and lactoferrin  $pI \approx 8$ ) resulting in oil  
602 droplets with different electrical charge versus pH profiles. Clusters were formed at pH values  
603 between the isoelectric points of the two single-protein emulsions where the two used proteins  
604 possessed opposite charges (Mao & McClements, 2011). Formation of mixed particle gels through  
605 heteroaggregation approach can provide highly viscous products at lower fat contents than in the  
606 absence of heteroaggregation (Mao & McClements, 2012b).

#### 607 **4. Conclusions**

608 Emulsion gel systems have advantages over conventional emulsions and hydrogels for certain  
609 applications, such as improved physical or chemical stability, texture modification, encapsulation  
610 of both lipophilic and hydrophilic components, and controlled release. Different methods by using  
611 several types of formulation additives have been employed for the manufacturing of emulsion gels.  
612 Physicochemical properties of emulsion gels which play an important role in determining their  
613 functional performance, are affected by employed fabrication method and formulation. The

614 embedding approach producing emulsion-filled gel systems allows the functional performance of  
615 the whole system e.g., the release of encapsulated components to be controlled via the  
616 manipulation of the composition, dimensions, permeability, and environmental responsiveness of  
617 the surrounding matrix. In situ-gelling approach provides injectable low viscosity fluids that can  
618 be introduced into the body prior to gelling within the desired tissue or organ. Clustering of  
619 droplets leading to formation of particle gels can be used to provide high viscosity and paste-like  
620 characteristics in some products or to control digestibility of lipids in the gastrointestinal tract.  
621 Formation of mixed particle gels through heteroaggregation can be a useful approach of creating  
622 products with novel textural characteristics or decreased fat contents. As well, encapsulation of  
623 two or more different lipophilic components within a single delivery system may be achieved via  
624 heteroaggregation approach. Considering the wide range of potential applications of emulsion gels  
625 in pharmaceutical, cosmetic and food industries, more studies are required in order to know the  
626 most appropriate conditions and ingredients needed to obtain the systems with specific functional  
627 attributes. As well, there is a need to carry out more studies to provide better understanding what  
628 happens to the emulsion gel systems during complex processes occurring within the human body.  
629 It could offer scientists the capability to design more effective functional systems with considering  
630 health-related aspects.

631

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901



## Figure captions

Fig. 1. Schematic representation of two emulsion-filled gels. a) oil droplets behave as active filler particles, b) oil droplets behave as inactive filler particles.

Fig. 2. Schematic representation of interactions between hydrophobically modified water-soluble polymers and surfactants. Inter-chain mixed aggregates formed at low surfactant concentration are progressively transformed into intra-chain mixed aggregates with increasing surfactant concentration (Kronberg et al., 2014).

Fig. 3. Schematic representation of two different matrix structures of emulsion-filled gels.

Fig.4. Schematic representation of a) fractal clusters of aggregated particles, b) network of fractal clusters (particle gel).

Figures

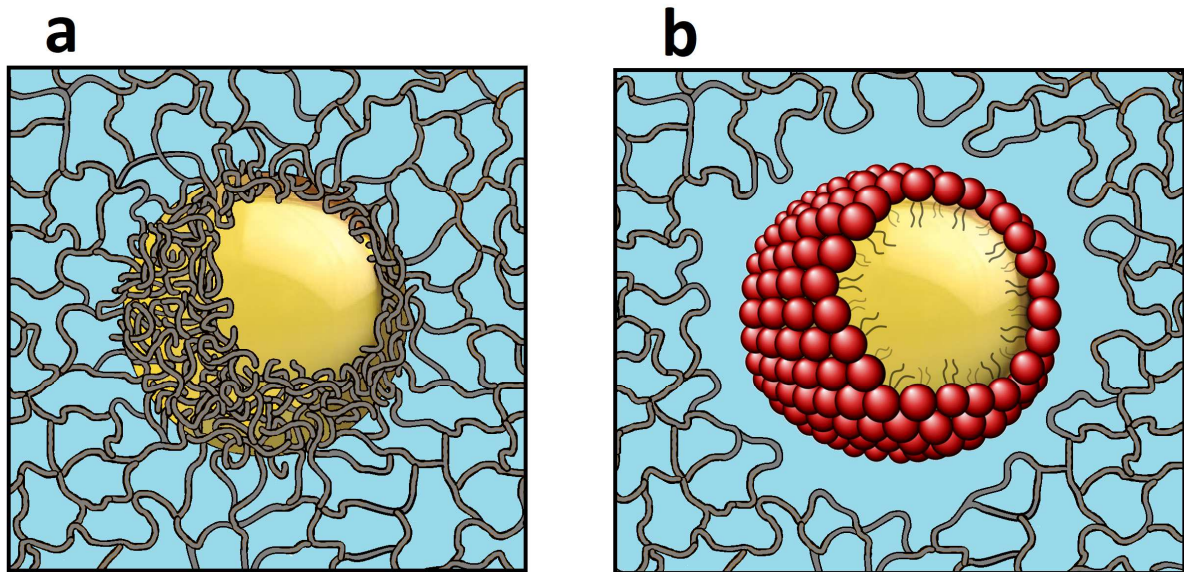
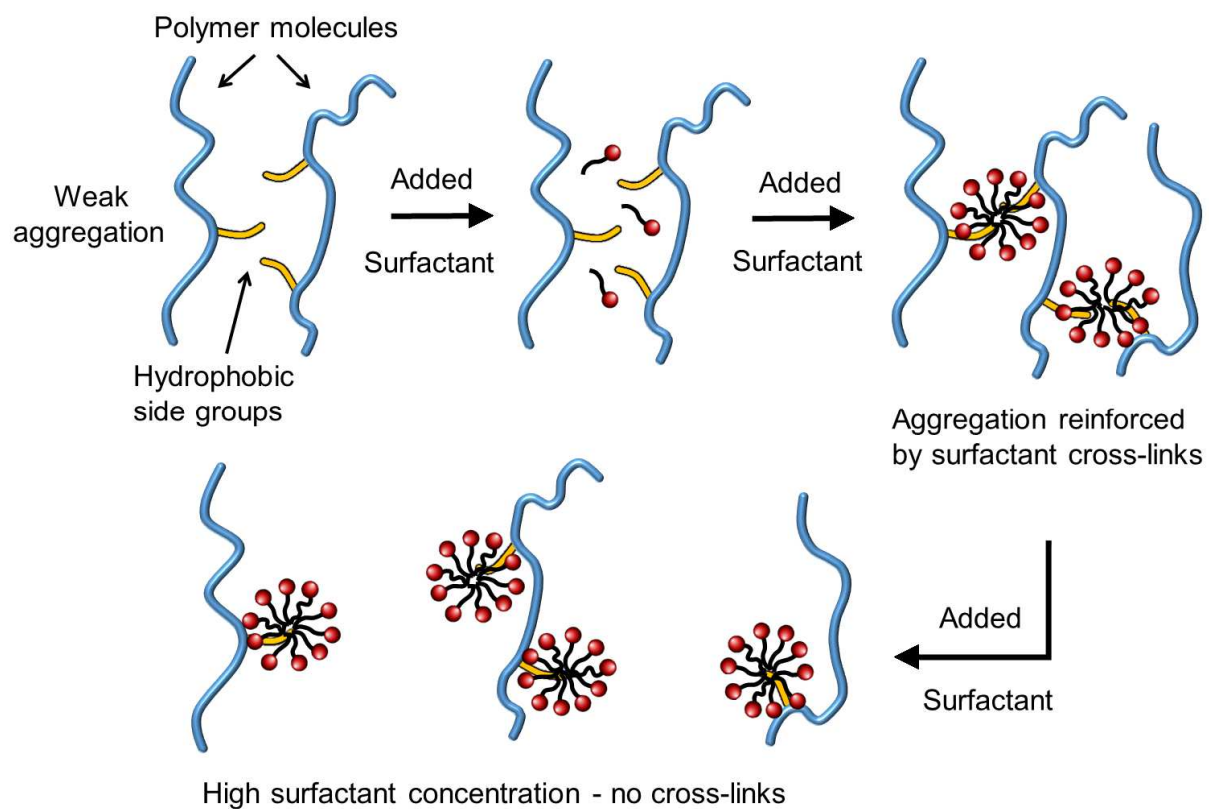
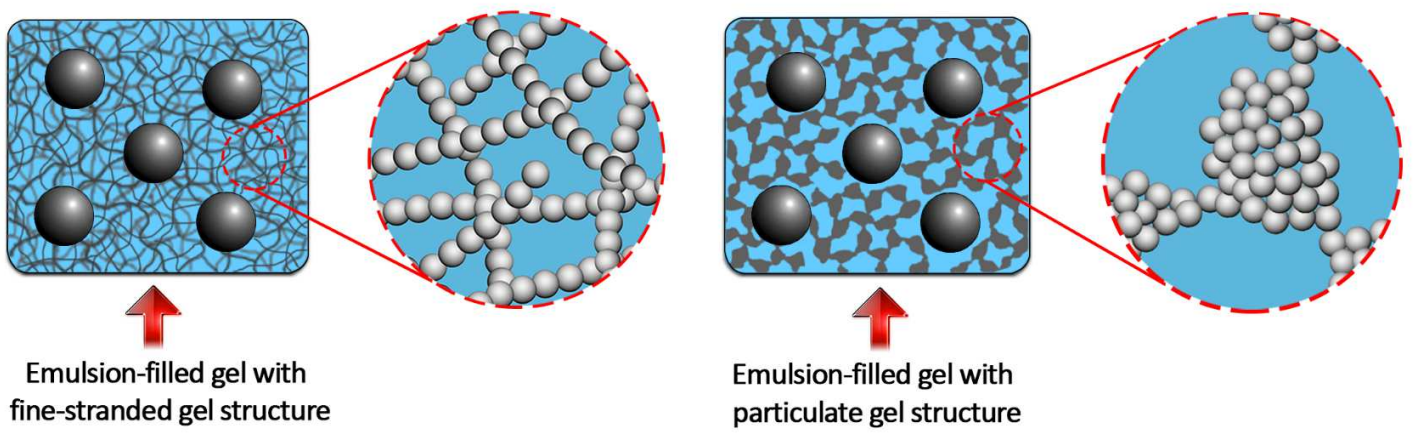


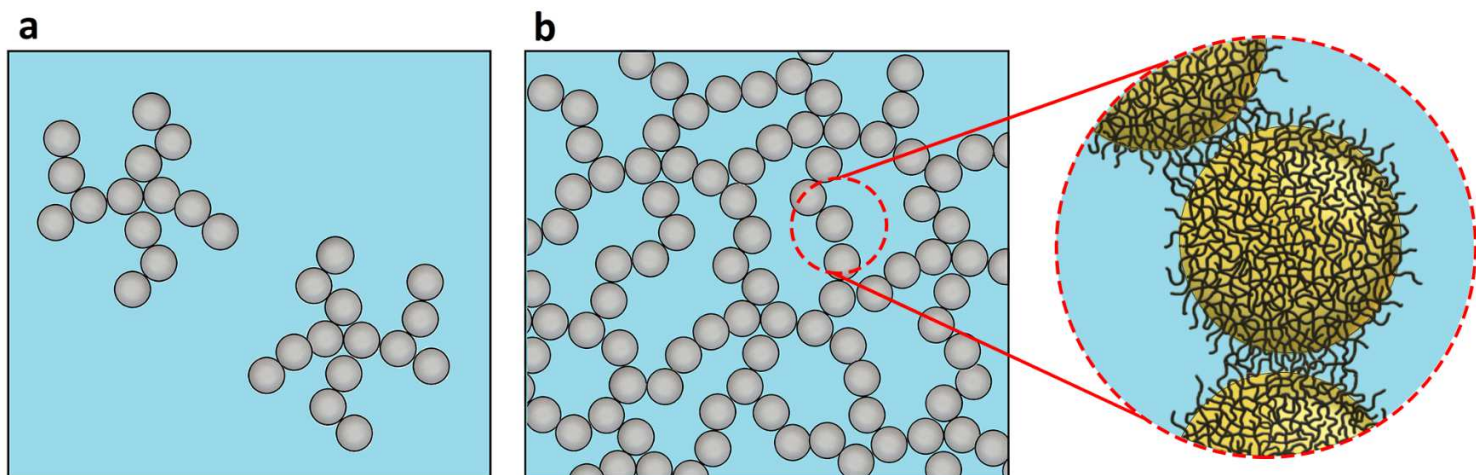
Fig. 1.



**Fig. 2.**



**Fig. 3.**



**Fig. 4.**

# Graphical Abstract

