



# Water-in-oil emulsions stabilized by surfactants, biopolymers and/or particles: a review

Morfo Zembyla, Brent S. Murray, Anwesha Sarkar\*

Food Colloids and Bioprocessing Group, School of Food Science and Nutrition, University of Leeds, Leeds, LS2 9JT, UK

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## ABSTRACT

**Background:** Considering the global rise of obesity and food-linked cardiovascular diseases, food industries are often challenged to produce low fat or fat-free products. Incorporation of water in the form of water-in-oil (W/O) emulsions to replace fat offers a promising strategy to address this research challenge.

**Scope and approach:** This review aims to provide succinct insights into the stabilization of W/O emulsions, focusing on interfacial design using surfactants, biopolymers, particles and/or combinations thereof that have been researched in the last decade. Particular emphasis has been given to particle (Pickering) stabilization of water droplets with bio-derived as well as non-bio-derived particles. In addition, the stabilization of W/O emulsions via viscosity modification is also briefly examined.

**Key findings and conclusions:** Although polyglycerol polyricinoleate (PGPR, E476) is considered as the ‘classic’ surfactant when it comes to stabilization of W/O emulsions, the focal point of current research has recently shifted towards the use of particle stabilizers that allow longer term stabilization against coalescence and Ostwald ripening. In particular, Pickering stabilizers that are derived from natural, biodegradable sources, such as zein, cellulose, lignin, starch and polyphenol crystals (curcumin and quercetin), with or without further modification, have attracted burgeoning attention due to the rising popularity of ‘clean-label’ products amongst consumers. Using such particles, or intelligently combining particles with biopolymers to stabilize high water volume fractions in oil continuous matrices, plus the use of biopolymers to gel the water phase, offer promising new applications in food and allied soft matter manufacturing areas in the future.

## 1. Introduction

A number of food-linked chronic diseases have been associated with the overconsumption of calorie-dense total fat, saturated fats, and trans-fatty acids, such as obesity, coronary heart disease, diabetes and hypertension (Abete, Goyenechea, Zulet, & Martinez, 2011; Dhaka, Gulia, Ahlawat, & Khatkar, 2011). Therefore, there has been considerable emphasis on the development of lipid-based food products with reduced levels of saturated, trans-fats and total fat (Nehir El & Simsek, 2012; Wassell, Bonwick, Smith, Almiron-Roig, & Young, 2010). One of the major challenges in developing these products is that fats play an important role in determining the desirable textural and sensory properties of many food products (Wassell, Bonwick, Smith, Almiron-Roig, & Young, 2010). Fat influences: (a) appearance (e.g., gloss, colour, translucency, surface uniformity, and crystallization); (b) texture (e.g., viscosity, elasticity, and hardness); (c) flavour (e.g., intensity of flavour, flavour release, flavour profile and flavour development); and (d)

mouthfeel (e.g., meltability, creaminess, lubricity, thickness, and degree of mouth-coating) of the final product (Patel, Nicholson, & Marangoni, 2020; Rios, Pessanha, Almeida, Viana, & Lannes, 2014).

Colloid scientists have attempted to identify or design “fat-replacers” that can mimic all of the different roles that fat plays in determining a product’s functional and sensorial properties (Marangoni, Van Duynhoven, Acevedo, Nicholson, & Patel, 2020; Patel et al., 2020). For instance, starch granules and microparticles of whey protein have been extensively reported as fat mimetics in literature (Chen et al., 2020; McClements, Chung, & Wu, 2017; Torres et al., 2018), but have showed limited success in mimicking some of the characteristic physicochemical properties of fat, such as mouthfeel, viscosity, and appearance (Marangoni et al., 2020; Patel et al., 2020).

Besides using fat mimetics, use of water to replace fat volume and lower the calorific content has been the most promising colloidal approach, usually in the form of water-in-oil (W/O) emulsion droplets. This method enables total fat content reduction, but also allows

\* Corresponding author.

E-mail address: [A.Sarkar@leeds.ac.uk](mailto:A.Sarkar@leeds.ac.uk) (A. Sarkar).

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**Table 1**  
List of surfactants, biopolymers or particles (bio-derived and non-bio-derived) used for stabilizing W/O emulsions.

Type	Emulsifier/Particle	Emulsifier/Particle concentration (wt. %)	Water volume fraction (vol %)	D <sub>3,2</sub> /μm	References	
<b>Surfactant</b>	PGPR	0.2–10	10–50	1–3	Chen, Rao, Ding, McClements, and Decker (2016); Dridi, Essafi, Gargouri, Leal-Calderon, and Cansell (2016); Killian and Coupland (2012); Márquez et al. (2010); Nazari, Mehrnia, Jooyandeh, and Barzegar (2019); Ushikubo and Cunha (2014); Wolf et al. (2013)	
	Span 20, 80, 85	0.001–12	10–50	0.05–1	Almeida et al. (2017); Koneva et al. (2017); Nazari et al. (2019); Pimentel-Moral, Rodríguez-Pérez, Segura-Carretero, and Martínez-Férez (2018); Politova, Tcholakova, Tsibranska, Denkov, and Muelheims (2017); Ushikubo and Cunha (2014)	
	Lecithin	0.1–6	30–40	4.3–6.8	Chen et al. (2016); Killian and Coupland (2012); Pan, Tomás, and Anón (2002); Ushikubo and Cunha (2014)	
	Ricinoleic acid ester (CR- 310)	1–5	10–30	0.2–6	Bhatti, Khalid, Uemura, Nakajima, and Kobayashi (2017); Khalid, Kobayashi, Neves, Uemura, and Nakajima (2013); Rabelo et al. (2018)	
<b>Biopolymer &amp; Surfactant</b>	Proteins (e.g., β-lactoglobulin, WPI, casein) & PGPR or Lecithin	0.5–8	2–40	0.5–6	Gülseren and Corredig (2012); Iqbal et al. (2012, 2013a, 2013b); Iqbal, Xu, Huang, and Chen (2019a); Wang et al. (2016); Yi, Zhu, McClements, and Decker (2014)	
	Polysaccharides (e.g., gelatine, pectin, xanthan, cellulose, κ-carrageenan, glycerol) & PGPR or Lecithin	2.5–16	30–80	0.2–6.5	Clausse, Lanoisellé, Pezron, and Saleh (2018); Gülseren and Corredig (2014); Iqbal, et al. (2019a, 2019b); Massel et al. (2015); Wardhono et al. (2014)	
<b>Particle</b> <sup>c</sup>	<b>Non-Bio-derived</b>	Silica (5–30 nm)	0.4–8	20–60	6–40	Ahuja, Iqbal, Iqbal, Lee, and Morris (2018); Drelich et al. (2010); Macedo Fernandes Barros, Chassenieux, Nicolai, de Souza Lima, and Benyahia (2018); Masalova and Kharatyan (2013); Nesterenko et al. (2014); Pichot, Spyropoulos, and Norton (2012); Santini, Guzmán, Ferrari, and Liggieri (2014); Skelton et al. (2012); Tshilumbu and Masalova (2015); Venkataramani, Smay, and Aichele (2016); Zhai et al. (2019) <sup>a,b</sup>
		<b>Bio-derived</b>	Latex (0.03–2.7 μm)	1.5–6	20–50	14–156
	Cellulose (20–200 nm)		3.8 × 10 <sup>3</sup> –3	20–89	27–250	Duffus et al. (2016); Guo et al. (2017); Hu, Ballinger, Pelton, and Cranston (2015); Lee, Blaker, Murakami, Heng, and Bismarck (2014); Lif, Stenstad, Syverud, Nydén, and Holmberg (2010); Pang et al. (2018); Rein, Khalfin, and Cohen (2012); Khanari, Syverud, and Stenius (2011) <sup>a</sup>
	Lignin (~20 μm)		8	50	100–300	Gould et al. (2016)
	Zein (180 nm)		2.5	10–30	~100	Rutkevicius et al. (2018)
	Starch (150 nm)		0.5–2	50	10–34	Zhai et al. (2019)
	Sunflower oleosomes (~1 μm)		0.5	10	5–20	Karefyllakis, Van Der Goot, and Nikiforidis (2019)
	Polyphenol crystals (0.2–4 μm)	0.14	5–20	7–25	Duffus et al. (2016); Zembyla, Lazidis, Murray, and Sarkar (2019); Zembyla, Murray, Radford, and Sarkar (2019); Zembyla et al. (2018) <sup>b</sup>	

<sup>a</sup> = In some studies, surfactants were used in combination with the particles.

<sup>b</sup> = In some studies, biopolymers were used in combination with the particles.

<sup>c</sup> = Mean size range of the particles are shown in parenthesis, for anisotropic particles, the smallest dimension of the width is reported.

incorporation of water soluble nutrients and flavourings in the aqueous phase for food, pharmaceutical and parenteral applications (Driscoll, 2017; Raman et al., 2017). Although this appears to be a promising strategy in theory, lack of stability of these W/O emulsion systems still presents a key challenge to their successful exploitation.

In this review, we therefore examine the recent advances in designing W/O emulsions focusing on advances in colloidal stabilization aspects. The emphasis is on W/O emulsions and does not include any specific discussion of multiple emulsions (e.g., water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) emulsions), although the conclusions might equally well be applied to the W/O component of these systems. A very recent review (Zhu et al., 2019) has also elegantly discussed the applications of W/O emulsions as fat replacers and delivery vehicles for water-soluble nutrients. The central focus is on the interfacial stabilization mechanisms of W/O emulsions rather than specific applications in food matrices. Particularly, we examine the various stabilizers (e.g., surfactants, biopolymer and/or particles) that have been used in the last decade to stabilize W/O emulsions and the pros and cons of each, on their own or in combination to create more complex

interfaces. We also compare the stability of emulsions stabilized by surfactants, biopolymers, particles that are either non-bio-derived or bio-derived and combinations thereof. Particular focus has been given to particle-stabilized (Pickering) W/O emulsions, due to their topical nature and their 'ultra-stability' - that has attracted much attention in the last decade. We have also examined strategies that have been used to modify the viscosity of the water or oil phase in order to improve W/O emulsion stability. Finally, we highlight the gaps in the literature to indicate the areas where future studies need to be conducted. Related reviews on polymeric microgels, fat crystals, oleogels or wax-stabilized emulsions (Dassanayake, Kodali, & Ueno, 2011; Dickinson, 2010; Ghosh & Rousseau, 2011; Murray, 2019a; Richtering, 2012; Sato & Ueno, 2011; Tang, Quinlan, & Tam, 2015) can be read elsewhere.

## 2. Emulsifiers and stabilizers

In order to prepare kinetically stable emulsions, an emulsifier is needed to protect the newly formed droplets against the different destabilization mechanisms. The emulsifier forms a protective

interfacial layer when it adsorbs to the surface of droplets, preventing the droplets from merging together. A ‘stabilizer’, on the other hand, tends to maintain the physicochemical state of an emulsion mainly by acting as a thickening agent, enhancing the viscosity of the continuous phase and consequently decreasing rate of droplet encounters and the sedimentation rate (Borreani, Leonardi, Moraga, Quiles, & Hernando, 2019). However, emulsifiers are also referred to as stabilizers. A range of emulsifiers can be used for generating W/O emulsions (see Table 1), as indicated schematically in Fig. 1a:

- low molecular weight surface active agents, commonly just referred to as surfactants, e.g., polyglycerol polyricinoleate (PGPR), sorbitan monooleate (commercially known as Span 80), lecithin, etc.;
- biopolymers, e.g., proteins or polysaccharides (usually with hydrophobic modification);
- insoluble particles, e.g., hydrophobic silica particles, latex particles, modified cellulose particles, polyphenol crystals, etc.;
- combinations of the above.

### 3. W/O emulsions stabilized by low molecular weight surfactants

As shown in Table 1, PGPR and lecithin have been mainly used to stabilize water droplets (up to 30 wt%) in soybean oil (Killian & Coupland, 2012). The PGPR-stabilized water droplets have been reported to be significantly smaller and more stable than the ones stabilized by lecithin, with the latter showing evidence of flocculation immediately after emulsification (Killian & Coupland, 2012). This was attributed to the ability of PGPR to form elastic interfaces that slow down the rate of coalescence between droplets (Killian & Coupland, 2012; Márquez, Medrano, Panizzolo, & Wagner, 2010). The properties of surfactant-stabilized W/O emulsions were strongly dependent on the lipid and emulsifier type used. Better chemical affinity between the hydrophobic moieties of the emulsifier and the oil lead to more stable water droplets. For instance, Ushikubo and Cunha (2014) evaluated the stability of W/O emulsions (30–40 vol% water) in the presence of different surfactants (PGPR, lecithin and Span 80) and oils (soybean oil and hexadecane). Emulsions with higher kinetic stability (>14 days) and smaller-sized water droplets ( $D_{4,3} = 1$  to 4  $\mu\text{m}$ ) were observed in the systems containing soybean oil and PGPR or hexadecane with Span 80. Both systems presented an interface with low initial interfacial tension (Ushikubo & Cunha, 2014).

Addition of salts (NaCl,  $\text{CaCl}_2$  up to 0.25 M) has been shown to improve the kinetic stability of PGPR-stabilized emulsions to coalescence, lowering the rate of Ostwald ripening as described earlier and decreasing the refractive index difference between oil and water phases (Israelachvili, 2015; Wolf, Koehler, & Schuchmann, 2013). Márquez et al. (2010) demonstrated the stabilizing effects of salt (up to 1 wt%  $\text{CaCl}_2$  in the aqueous phase) in the emulsions stabilized by PGPR (up to 1 wt%) – resulting in a decrease of the mean particle size ( $d_{43}$ ) from 6 to

1  $\mu\text{m}$  and higher stability. The higher stability in presence of calcium salts was attributed to a lower attractive force between water droplets and a higher adsorption density of the emulsifier, manifested by a lower interfacial tension (Márquez et al., 2010). According to Israelachvili (2015), the attractive force (due to van der Waals interactions) between two water droplets in the oil continuous phase (e.g., mineral oil) is at a minimum when the refractive indices and/or the dielectric constants of the two phases are matched. Thus, the addition of calcium salt into the water phase would decrease the attractive force between water droplets, reducing the collision frequency. In this way, calcium salts would allow the production of W/O emulsions with higher stability to coalescence and, consequently, sedimentation (Israelachvili, 2015; Márquez et al., 2010).

Although from functional point of view these low molecular weight surfactants have been successful in providing many emulsions with sufficient kinetic stability, there has been increasing work in recent years to improve and understand the stability offered by more ‘clean-label’ emulsifiers, for example those based on biopolymers such as proteins, starches and non-starch polysaccharides, either alone or use combination with other surfactants. This is discussed in the next section.

### 4. W/O emulsions stabilized by biopolymers

A biopolymer can be incorporated into the surface of emulsion droplets in two ways, depending on whether the biopolymer is surface active (most proteins) or non-surface active (most polysaccharides) (Dickinson, 2011). Therefore, they are associated with the interfacial region either by:

- adsorption directly to the interface during droplet formation and stabilization, or
- interaction with another surfactant or biopolymer layer, which is already located at the interface (Dickinson, 2011).

All proteins contain both hydrophilic and hydrophobic regions along their backbones, whereas only a limited number of natural polysaccharides have non-polar side chains attached to their polar backbones (McClements, 2015). Some polysaccharide chains that are largely hydrophilic may contain small amounts of protein ‘impurities’ that impart surface activity (Osano, Matia-Merino, Hosseini-Parvar, Golding, & Goh, 2010). Although there has been significant amount of work on stabilizing O/W emulsions with proteins and polysaccharides, to our knowledge there has been no study that has demonstrated stabilization of W/O emulsions by a biopolymer interfacial layer on its own. Therefore, combinations of biopolymers and surfactants are discussed in this section.

Biopolymers have been mainly used in W/O emulsions as viscosity-modifiers of the aqueous phase, which tends to improve the kinetic stability of the droplets whilst the primary emulsifying agent is some other species, usually a low molecular weight surfactant. The aqueous

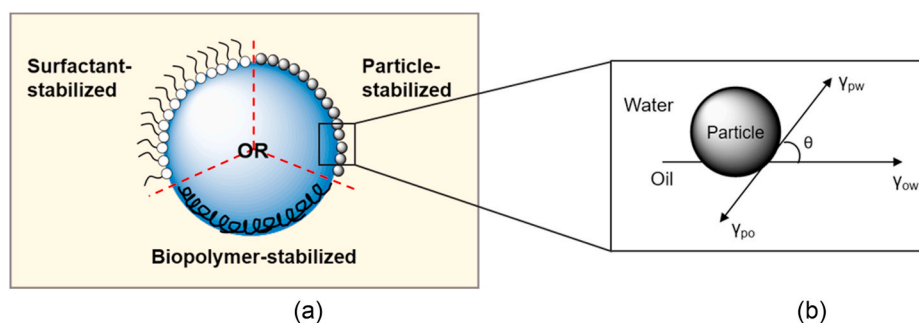


Fig. 1. (a) Schematic diagram of a W/O emulsion droplet showing different interfacial stabilization by surfactant, biopolymers or particles. (b) The three-phase contact angle is related to the balance of surface free energies at the particle-water, particle-oil and water-oil interfaces.

phase viscosity modifier can be almost any thickening or gelling agent, e. g., whey protein isolate (WPI) (Iqbal, Hameed, Baloch, & McClements, 2012; Zhu et al., 2015), sodium caseinate (Wang et al., 2016), pectin (Gülseren & Corredig, 2014), lactoferrin (Iqbal, Hameed, Baloch, & McClements, 2013b) or  $\beta$ -lactoglobulin (Gülseren & Corredig, 2012; Iqbal et al., 2013b), combined with PGPR for instance – see Table 1.

Massel, Alexander, and Corredig (2015) demonstrated that the presence of high methoxy (HMP) or low methoxy pectin (LMP) in the aqueous phase of PGPR-stabilized W/O emulsions caused the formation of smaller water droplets (~305 and 317 nm for HPM and LMP, respectively) and more stable emulsions than the same PGPR-stabilized emulsion without pectin (~440 nm).

Proteins can thicken and gel the aqueous phase by employing suitable processing treatments, such as heat treatment to denature whey proteins (Gülseren & Corredig, 2012; Iqbal et al., 2012) or acidic treatment to gel caseinate (Wang et al., 2016). Using their WPI system, Iqbal et al. (2012) showed that the ‘solidified’ droplets, or microspheres, formed a three-dimensional network in the oil phase, allowing up to 30 wt% water in the system. The emulsions exhibited a non-ideal plastic behaviour: they were solid-like at low stress, fluid-like (shear-thinning) at intermediate stresses, but became disrupted (exhibiting excessive aggregation and phase separation) at high stresses (shear rate  $\sim 20 \text{ s}^{-1}$ ) (Iqbal et al., 2012). In a different study, casein dispersions containing glucono- $\delta$ -lactone (GDL) and soybean oil with PGPR were homogenized to form W/O emulsions (Wang et al., 2016). GDL was hydrolyzed to gluconic acid inside the aqueous phase, causing a gradual reduction on the pH value. When the pH reached the isoelectric point of casein (pI = 4.6), gelation of the inner aqueous phase occurred (Wang et al., 2016). The GDL-induced casein gels in the inner aqueous phase provided higher resistance to destabilization as compared to that of the non-gelled W/O emulsions. In addition, the size of the emulsions formulated by the gelled aqueous phase and 2 wt% PGPR remained smaller (~649 nm) even after 90 days of storage than the emulsions with 6 wt% PGPR in the absence of gelling of the aqueous phase by GDL (~1128 nm, after 90 days) (Wang et al., 2016).

## 5. Stabilization of W/O emulsions by particles (Pickering emulsions)

The term ‘Pickering stabilization’ is used for stabilization of droplets using fine insoluble solid particles that provide ‘ultrastability’ to emulsions (Pickering, 1907; Tambe & Sharma, 1994). Finkle, Draper, and Hildebrand (1923) stated that in an emulsion containing solid particles, the liquid which wets the solid less than the other liquid will be the dispersed phase, which in effect is in agreement with Bancroft’s rule, that states that “in order to have a stable emulsion, the emulsifier must have a relatively high dispersibility in the continuous phase” (Tsabet & Fradette, 2015). In addition, there can be sintering of the particles at the interface (Ngai & Bon, 2014) that leads to a solid shell or ‘armoured’ droplets. Solid particles not attached to the interface can additionally form a network in the bulk continuous phase (Ghosh, Tran, & Rousseau, 2011; Sarkar & Dickinson, 2020) and so provide another mechanism to prevent water droplet collisions, sedimentation and coalescence - hence the term network stabilization that has attracted significant attention in the literature (Ngai & Bon, 2014), though this essentially the same as the parallel stabilizing effects of flocculation observed in O/W emulsions. Effective Pickering stabilization can only be achieved when the average size of adsorbed particles is at least an order of magnitude smaller than the emulsion droplet size (Dickinson, 2012).

The three phase particle contact angle ( $\theta$ ), describes the wettability of the particle at the interface and whether the particle prefers to reside in the water or oil phase. By convention,  $\theta$  is measured in the aqueous phase (see Fig. 1b) and so if  $\theta < 90^\circ$  then a larger fraction of the particle surface resides in aqueous than in the non-polar phase, i.e., the particle is relatively hydrophilic and so will tend to stabilize an O/W emulsion. Conversely, if  $\theta > 90^\circ$  the particle is more hydrophobic and will tend to

stabilize a W/O emulsion (particles wetted equally by oil and water have contact angle exactly  $90^\circ$ ). The value of  $\theta$  is related to the balance of surface free energies at the particle-water ( $\gamma_{pw}$ ), particle-oil ( $\gamma_{po}$ ) and oil-water ( $\gamma_{ow}$ ) interfaces and is expressed by the classic Young’s equation (equation (2)) (Binks & Horozov, 2006, pp. 1–74; Dickinson, 2012).

$$\cos(\theta) = \frac{(\gamma_{po} - \gamma_{pw})}{\gamma_{ow}} \quad (2)$$

Depending on the size and contact angle that the particles have at the W–O interface, the energy of attachment (see below) may exceed thousands of  $k_B T$  and thus particle adsorption is virtually irreversible (Ettelaie & Lishchuk, 2015; Murray, 2019b; Sarkar, Zhang, Holmes, & Ettelaie, 2018). This high detachment energy is the reason for the ‘ultrastability’ of particle-stabilized emulsions compared to conventional surfactant-stabilized systems.

The minimum energy of detachment, or desorption, ( $\Delta G_d$ ) of a spherical particle is given by:

$$\Delta G_d = \pi r^2 \gamma_{ow} (1 \pm \cos(\theta))^2 \quad (3)$$

where  $\gamma_{ow}$  is the interfacial tension between the oil and water phases;  $\theta$  is the particle contact angle (the sign inside the bracket is negative if the particle is removed into the aqueous phase and positive if it is removed into the oil phase);  $r$  is the particle radius. Thus,  $\Delta G_d$  is directly proportional to the interfacial tension ( $\gamma_{ow}$ ) and the square of the size of the particles and reaches a maximum when  $\theta = 90^\circ$ .

Conventionally, ‘non-bio-derived’ synthetic particles, such as hydrophobic silica, polystyrene latex, etc., have been described in the literature for stabilizing W/O emulsions. Many of these emulsions have much higher droplet sizes compared to surfactant-stabilized emulsions (see Table 1) – because the particle size is much larger than typical nanometre-sized surfactant molecules. Lately, however, there has been a growing search for bio-based particles or the creation of natural particles by some physical or chemical modification, due to increasing demands for ‘clean-label’ stabilizers of W/O emulsions, as discussed in the Introduction. Recently, cellulose, lignin, starch, zein and polyphenol particles have surfaced in the literature as surfactant-free Pickering emulsion stabilizers. Hence, in this section, W/O emulsions have been categorized into those stabilized by conventional non-bio-derived particles and the others stabilized by bio-derived particles. Also, recent studies on W/O emulsions stabilized by a combination of particles and surfactants and/or biopolymers are examined.

### 5.1. Non-bio-derived particles

#### 5.1.1. Silica particles

The most commonly used particles used in Pickering emulsions are silica particles. Fumed silica particles can be made hydrophobic to varying degrees by reacting their surface silanols with organic silylating reagents. In this way it has been possible to quantitatively demonstrate the relationship between the stability as well as the type of emulsion formed and the hydrophobicity (contact angle) of the particles in the continuous phase (Yan, Gray, & Masliyah, 2001). For instance, when hydrophilic particles ( $\theta = 0^\circ$  or  $\theta = 60^\circ$ ) were used, no W/O emulsions formed, and most of the particles remained into the water phase (Yan et al., 2001). When the particles were made hydrophobic ( $\theta = 67^\circ$  or  $\theta = 75^\circ$ ), all the water (20 vol%) in the system became dispersed as very stable W/O emulsions droplets, generating mean water droplet diameter as small as  $2 \mu\text{m}$  (Yan et al., 2001).

Hydrophobic silica particles are often partially flocculated (Masalova & Kharatyan, 2013; Nesterenko, Drelich, Lu, Clause, & Pezron, 2014). Solid hydrophobic silica particles can efficiently stabilize W/O emulsion droplets (easily up to 30 wt% water) by forming a three-dimensional network in the continuous oil phase and so prevent droplet coalescence. No interfacial tension reduction is observed at the W–O interface in the presence of such particles (Drelich, Gomez,

Clause, & Pezron, 2010). Addition of surfactant - Span 80 or sorbitan monooleate (SMO) - to the oil phase of particle-stabilized W/O emulsions has been used to decrease the interfacial tension and aid stabilization, which implies the co-existence and therefore possibly interactions between the particles and emulsifiers at the interface (Drelich et al., 2010; Masalova & Kharatyan, 2013; Nesterenko et al., 2014; Tshilumbu & Masalova, 2015). The presence of closely packed aggregates around large droplets in emulsions stabilized by a small amount of surfactant (0.1 wt%) and silica particles (1.8 wt%) showed an improvement in the stability of the droplets up to 21 days, without any indication of phase separation (Nesterenko et al., 2014). However, emulsions prepared solely by silica particles showed oil separation after 21 days and the droplets were larger in size (~13  $\mu\text{m}$ ) compared to those in the presence of surfactants (~4  $\mu\text{m}$ ), probably due to the ability of surfactant molecules to adsorb onto the particle surface prior to the emulsification. The stability enhancement was more pronounced at low surfactant concentrations, where particles could compete effectively for the interface. However, another contribution to the stability could have been the unadsorbed particles forming a flocculated network in the oil continuous phase (Masalova & Kharatyan, 2013; Nesterenko et al., 2014).

Similar to biopolymer + surfactant systems, research has illustrated the ability of biopolymers to improve the stability of silica-stabilized Pickering W/O emulsions, where the biopolymers mostly act as gelling agents in the water phase. For instance, Skelhon, Grossiord, Morgan, and Bon (2012) investigated the stability of W/O emulsions using hydrophobic fumed silica particles in combination with chitosan, of low and medium molecular weight (75–85% de-acetylated chitosan) under acidic conditions (pH 3.2–3.8). Adsorption of the oppositely charged chitosan onto the surface of the negatively charged silica particles changed the particle wettability so that it was a much more effective Pickering stabilizer (Skelhon et al., 2012). As the concentration of silica particles was increased from 0.6 to 5.3 wt%, at a constant concentration of chitosan (1 wt%), a continuous network of colloidal flocs was formed, immobilizing the water droplets. The viscosity of the whole emulsion system increased from 690 to ~2000 mPa s when the chitosan concentration increased from 0 to 1 wt%. Zhai et al. (2019) demonstrated that combining silicones (SO), modified silicones (DC8500) and starch in the dispersed phase enabled the formation of high internal phase emulsions containing up to 83 vol% water that were stable for more than 6 months. Without the addition of starch, the water content of stable emulsions could only be raised up to 20 vol% (Zhao et al., 2019).

### 5.1.2. Latex particles

Organic latex particles, which are probably the most widespread type of monodisperse colloids, have found a relative narrow range of application as emulsifiers. The reason seems to be that, under normal conditions, latex particles do not adsorb well at the W–O interface. Latex particles tend to be hydrophobic, even though they are synthesized and dispersed in water due to the ionisable surface sulfate groups, and can stabilize W/O emulsions (Binks & Lumsdon, 2001). This appears to oppose Bancroft's rule. Although this rule works very well for surfactant-stabilized emulsions, in the case of Pickering emulsions, the stability is ensured by the formation of a dense (shell-like) particle adsorption layer, irrespective of which phase the particles originate from.

Stable W/O emulsions (up to  $\phi = 0.2$ ) were formed by using a combination of positively-charged (size: 2.2  $\mu\text{m}$ ) and negatively-charged (size: 3.0  $\mu\text{m}$ ) monodisperse surfactant-free polystyrene latex particles, functionalized by amidine and sulfate groups (dispersed in water), respectively (Nallamilli, Binks, Mani, & Basavaraj, 2015). The contact angles of amidine and sulfate polystyrene particles were around 103.1° and 116.1°, respectively. Charged particles of one type alone were not able to stabilize emulsions due to repulsive interactions. However, when these oppositely charged particles were mixed, they formed aggregates, and were able to adsorb at the interface and stabilize W/O emulsions.

However, the size of the water droplets stabilized by these aggregated latex particles was very large (~400  $\mu\text{m}$ ), thus they were not desirable in products due to their potential instability under different processing conditions (Nallamilli et al., 2015).

## 5.2. Bio-derived particles

Although there has been lot of emphasis recently in trying to find bio-derived particles, most of the particles discussed in literature are modified using some sort of chemical/physical treatment or complex formation with other surfactants/biopolymers/particles, in order to increase their effectiveness as Pickering stabilizers.

### 5.2.1. Modified cellulose

Cellulose is the most abundant biopolymer in nature. It is biodegradable and renewable and possesses some very interesting chemical and physical properties (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Siró & Plackett, 2010). In the native state, cellulose consists of long chains of poly- $\beta$ -(1  $\rightarrow$  4)-D-glucosyl residues (Andresen & Stenius, 2007). During biosynthesis, these chains aggregate to form microfibrils, which are long, thread-like, highly crystalline bundles of molecules stabilized laterally by intermolecular hydrogen bonds. The production of nanoscale cellulose fibers and their application in composite materials has gained increasing attention due to their high strength and stiffness combined with low weight, biodegradability and renewability (Siró & Plackett, 2010).

Due to the hydrophilic nature of the cellulose molecules, the fibrils, microfibrils and nanocrystalline cellulose are better wetted by water than oil, and therefore tend to stabilize water-continuous emulsions (Du Le, Loveday, Singh, & Sarkar, 2020). Pang, Liu, Liu, Peng, and Zhang (2018) synthesized hydrophobically modified microcrystalline cellulose via stearoylation (with stearoyl chloride) to produce a stearoylated microcrystalline cellulose (SMCC) with a static water contact angle at 108.2°. Pickering W/O emulsions were prepared by using 0.5 wt% SMCC and the droplet size ranged from 10 to 120  $\mu\text{m}$ . Although sedimentation was observed, no coalescence was found during storage of more than two months, highlighting the highly effective Pickering stabilization by this modified cellulose (Pang et al., 2018).

Guo, Du, Gao, Cao, and Yin (2017) prepared a novel W/O Pickering emulsifier through the fabrication of cellulose nanocrystals (CNCs), prepared by acid hydrolysis of cellulose under ultrasonic treatment, by substituting some of the CNC hydroxyl groups with alkyl groups via a chemical reaction with n-octadecyl isocyanate. Alkyl-intercalated CNCs with different particle lengths (77–84 nm) failed to stabilize W/O emulsions if the hydroxyl groups were fully substituted with alkyl groups but alkyl-intercalated CNCs with intermediate degrees of substitution possessed good emulsifying capacity (Guo et al., 2017). Results showed that alkyl-intercalated CNCs with different degrees of substitution gave similar interfacial tensions, possessed similar molecular arrangement of internal intercalated alkyls, but exhibited different contact angles (Guo et al., 2017), ranging between 124 and 147°. Increasing degree of substitution gave larger contact angles and increasing ease of dispersibility in the oil phase (Guo et al., 2017).

### 5.2.2. Lignin

Lignin is also an extremely abundant terrestrial biopolymer, accounting for approximately 30% of the organic carbon in the biosphere (Thakur & Thakur, 2015). It is characterized by its highly branched heterogeneous structure, built from cross-linking various phenolic residues (Gould, Garcia-Garcia, & Wolf, 2016). Lignin is key in imparting rigidity to the secondary cell walls of plant cells and the stiffness and strength of stems, etc. In addition, lignin acts as a waterproof coating to the cell wall, enabling transport of water and solutes through the vascular system, and plays a role in protecting plants against pathogens (Thakur & Thakur, 2015). Ground coffee waste is rich in lignin and has been investigated as a potential Pickering stabilizer. Hydrothermal

treatment of lignin, adapted from the bioenergy field, has been used to generate lignin particles capable of stabilizing W/O emulsions (Gould et al., 2016). The hydrothermal treatment (heating at 150–275 °C for 1 h, immersion in cold water, filtration and drying in a convection oven at 40 °C for 48 h) caused relocation of the lignin components present in the cell walls onto the particle surface in the form of droplets, increasing the surface hydrophobicity of the particles (Gould et al., 2016). Emulsions stabilized by lignin particles (8 wt%) showed an intermediate stage of coalescence – termed arrested coalescence (Gould et al., 2016). However, the W/O emulsions were not analysed further because the large water droplet size (100–300 µm). The hydrothermally-treated waste coffee particles were not desirable in food products due to their potential instability towards shear and mixing processes (Gould et al., 2016).

### 5.2.3. Modified starch granules

Starch is a natural, renewable, and biodegradable polymer produced by many plants as a source of stored energy (Le Corre, Bras, & Dufresne, 2010). Starch, of course, consists of two distinct molecules: amylose, a linear polymer of  $\alpha$ -D-glucose linked by 1 → 4 glycosidic linkages, and amylopectin, a much larger, branched polymer of  $\alpha$ -D-glucose with 1 → 4 and 1 → 6 (branching) linkages (Singh, Dartois, & Kaur, 2010). Starch in nature is structurally arranged in the form of granules, that are partly crystalline and range in size from ~1–100 µm, depending upon their biological origin (Borah, Rappolt, Duary, & Sarkar, 2019).

Similar to cellulosic particles, starch granules have been widely investigated as O/W emulsion stabilizers (Marku, Wahlgren, Rayner, Sjöo, & Timgren, 2012; Timgren, Rayner, Sjöo, & Dejmeck, 2011; Zhu, 2019) due to their inherent hydrophilic nature. However, very recently, corn starch was esterified by p-toluenesulfonyl chloride (TS) and palmitoyl chloride (PA) (Zhai et al., 2019) to create hydrophobic starch ester-based nanoparticles. The particles were dispersed in ethyl acetate and were ~150 nm in size, where they were used to stabilize water droplets in the ethyl acetate-starch dispersion. The palmitoyl groups apparently imparted sufficient hydrophobicity to the resultant starch ester nanoparticles to avoid their aggregation and collapse in ethyl acetate. If the starch was modified only by PA, no stable W/O emulsions were obtained, probably because the particles were too hydrophobic to remain at the interface. The TS attached to the starch backbone and were rendered some degree of hydrophobicity, coupled with the relatively hydrophilic tosylate groups (Zhai et al., 2019). The average size of the water droplets was ~34 µm when the nanoparticle concentration was 0.5 wt%, and decreased to ~10 µm with an increase in the nanoparticle concentration to 2 wt% (at a water volume fraction below 50 wt%). Consequently, the stability of the emulsions increased with increasing concentration of these starch-based nanoparticles (Zhai et al., 2019). However, this is an example of chemical modification that is hardly ‘clean-label’ and unlikely to be permitted in foods.

### 5.2.4. Zein particles

The storage proteins of maize seeds are alcohol-soluble prolamine-rich proteins that are collectively known as zein (Kasaai, 2018; Pascoli, de Lima, & Fraceto, 2018). Their only known function is to store nitrogen for the developing seed (Kasaai, 2018; Pascoli et al., 2018). Zein is one of the few naturally hydrophobic, water-insoluble proteins which have been approved for oral use by Food and Drug Administration (Patel & Velikov, 2014). The hydrophobicity of zein is attributed to the high percentage of non-polar amino acids (leucine, alanine and proline), which together makes up more than 50% of its total amino acid content and its highly aggregated structure (Patel & Velikov, 2014).

Rutkevicius, Allred, Velev, and Velikov (2018) investigated the ability of zein particles (~180 nm, not modified) to stabilize oil continuous emulsions. It was found that zein colloidal particle dispersions in water (i.e., not dispersed in the oil phase) at pH 4.0, blended with soybean oil, produced W/O emulsions with a water content up to 30 vol%, although the water droplets were large (~100 µm) and only stable for ~1 h (Rutkevicius et al., 2018). The zein particles were seen to

form networks within the water droplets, as observed from cryo-SEM images (Fig. 2a), aiding the stability of the droplets via viscosification of the droplet phase. The use of a particle dispersion at pH = 6.5 (zein’s isoelectric point) prior to emulsification, destabilized the suspension due to lower electrostatic repulsion between the particles, which led to particle aggregation and then the emulsions were stable only for few minutes (Rutkevicius et al., 2018). However, addition of lecithin into the oil phase (prior to emulsification) enhanced the hydrophobic character of zein particles, improved the stability of W/O emulsions (~100 µm) up to 1 day and allowed an increase in the dispersed water content to 40 vol % (Rutkevicius et al., 2018).

### 5.2.5. Polyphenol crystals

More recently, Pickering W/O emulsions have been prepared with a different kind of naturally occurring water-insoluble particle, namely polyphenol crystals (Duffus, Norton, Smith, Norton, & Spyropoulos, 2016; Zembyla, Lazidis, Murray, & Sarkar, 2019; Zembyla, Murray, Radford, & Sarkar, 2019; Zembyla, Murray, & Sarkar, 2018). Crystals of curcumin and quercetin (with three phase water contact angles ( $\theta$ ) of 175.3° and 80.9°, respectively) were shown to act as Pickering stabilizers of water in sunflower oil emulsions. Fig. 2b illustrates quercetin forming a layer of rod-shaped particles at the water droplet surface (Zembyla et al., 2018). In this study Zembyla et al. (2018) showed that both curcumin and quercetin on their own allowed stabilization of water droplets up to 5 wt% water without any modification of these particles (Fig. 3ai and 3bi). However, a marked improvement in the kinetic stability of the systems was achieved when 0.5 wt% WPI was added into the aqueous phase at pH 3.0 (Fig. 3aii and 3bii) (Zembyla, Murray, et al., 2019). This WPI concentration was far too low to induce droplet gelation, but created an electrostatic complex at the interface between polyphenol crystals (negatively charged) adsorbing from the oil side of the interface and the WPI (positively charged) adsorbing from the aqueous side. Further evidence for this complex formation was obtained from measurements of the interfacial shear viscosity. It was seen that the interfacial shear viscosity was enhanced three-fold (500–1500 mN s m<sup>-1</sup>) in the case of quercetin and six-fold (5–30 mN s m<sup>-1</sup>) in the case of curcumin, on addition of 0.5 wt% WPI (Zembyla, Murray, et al., 2019). The electrostatic nature of the complex was further confirmed by addition of salt: even a very low concentration of NaCl (0.001 M) caused a two-fold decrease in the interfacial shear viscosity for both the curcumin and quercetin + WPI systems.

The use of such oil-dispersible organic crystals plus the appropriate protein in the water droplets apparently has not been studied before, but is another example of how combinations of particles and biopolymers can be advantageous. A further big improvement water content (up to 20 wt%) and droplet stability up to 90 days was demonstrated by replacing the WPI with whey protein microgel (WPM) particles – creating a sort of “double” Pickering stabilization (see Fig. 3aiii and 3biii) (Zembyla, Lazidis, et al., 2019). In other words, the enhanced stability was attributed to electrostatic complexes forming between polyphenol Pickering particles adsorbing from the oil side and WPM Pickering particles co-adsorbing synergistically from the water side of the interface. However, at a higher concentrations of WPM particles ( $\geq 1.0$  wt%), WPM appeared as co-aggregates with polyphenol crystals and possibly some very small water droplets on the oil side of the interface. Therefore, in common with many other W/O stabilizing systems that have been proposed, some element of the initial emulsion stabilization may originate from aggregation of components in the oil phase (Zembyla, Lazidis, et al., 2019). Very recent work (Zembyla, Lazidis, Murray, & Sarkar, 2020), however, has shown that subsequent shearing and/or heating of these same WPM + polyphenol-stabilized W/O emulsions disrupts these aggregates in the oil phase but the W/O emulsions remain stable.

In spite of some of the outstanding issues and complications, many of the above studies suggest that there is good promise that bio-derived and naturally occurring biocompatible particles can be developed to stabilize W/O emulsions in practice. It is seen that combinations of

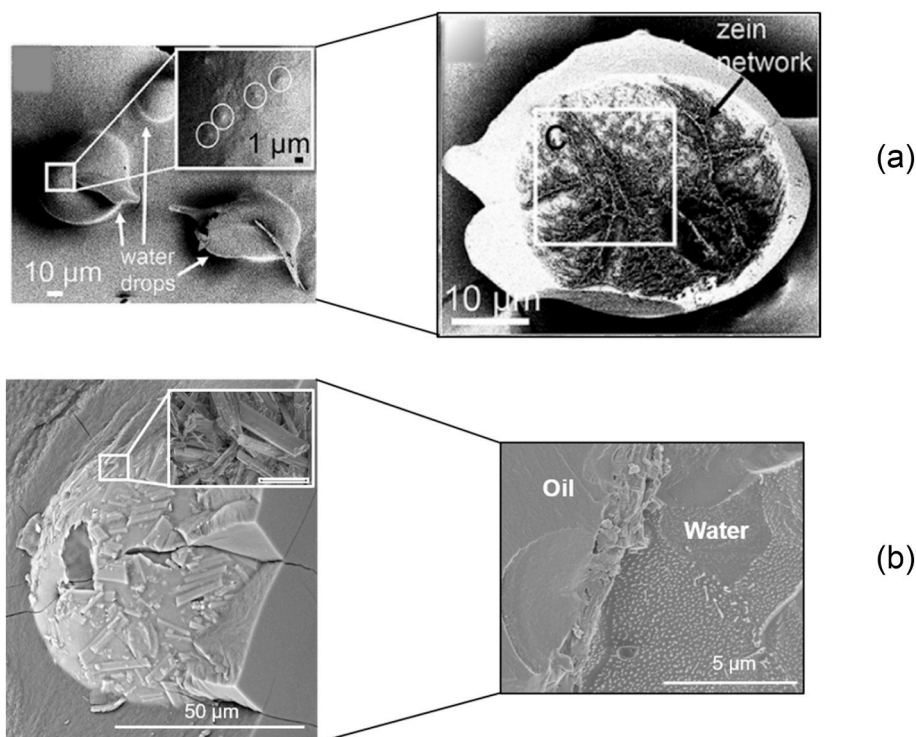


Fig. 2. Cryo-SEM images of W/O emulsions stabilized with (a) zein particles, reproduced with permission from Rutkevičius et al. (2018), Elsevier, and (b) emulsions stabilized by quercetin crystals, reproduced with permission from Zembyla et al. (2018), ACS and Sarkar and Dickinson (2020), Elsevier.

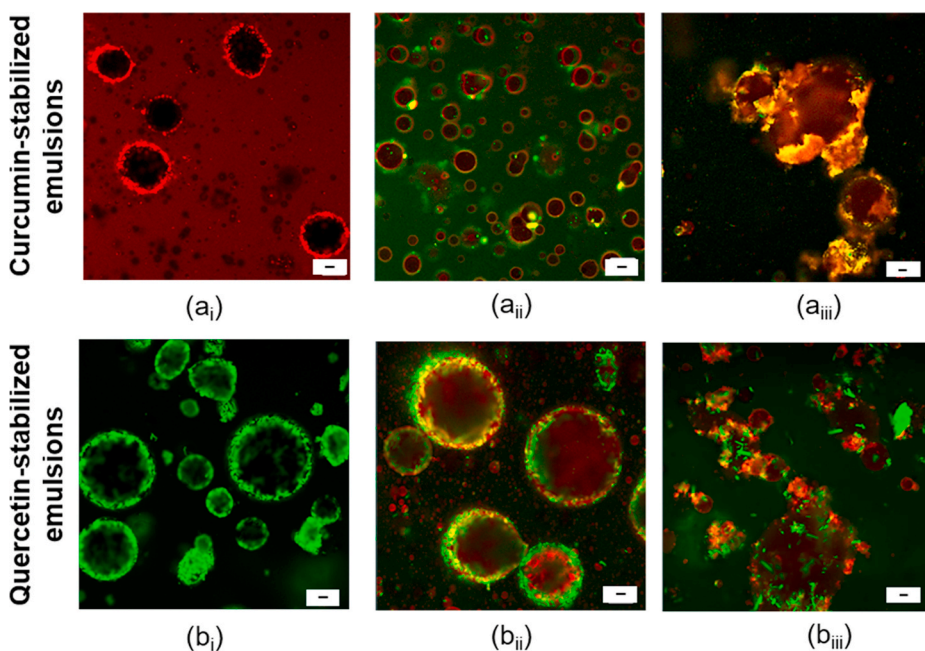


Fig. 3. Confocal images of fresh 10 wt% W/O Pickering emulsions stabilized by (a) 0.14 wt% curcumin or (b) 0.14 wt% quercetin crystals in the oil phase. The aqueous phase is (i) water, (ii) 2.0 wt% WPI or (iii) 2.0 wt% WPM particles at pH 3.0. The green brightness in the images is caused by the auto-fluorescence of curcumin (488 nm excitation) or quercetin (405 nm excitation) crystals. The red brightness is due to the WPM particles stained by Rhodamine B (568 nm excitation). The scale bar represents 20 μm. Reproduced with permission from Zembyla et al. (2018), Zembyla, Murray, et al. (2019), Zembyla, Lazidis, et al. (2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

biopolymers or biopolymeric particles might be most effective and this requires further investigation.

## 6. Rheological properties of W/O emulsions

Rheology plays a key role in food manufacturing, e.g., during material handling and processing, in quality control and the sensory aspects of oral and non-oral evaluation of viscosity (Rao, 2010). The rheology of food emulsions is fundamental to their properties and often related to

their stability (Gallegos, Franco, & Partal, 2004). In general, emulsion stability depends on droplet size distribution, rheology of the continuous phase and inter-particle interactions, temperature and water volume fraction. All these factors are strongly influenced by processing conditions, such as energy input during emulsification, residence time, application of thermal treatments, mixing efficiency, etc. (Gallegos et al., 2004). Emulsions for industrial application are compositionally and structurally complex materials which can exhibit a wide range of different rheological behaviours, ranging from low-viscosity fluids (e.g.,

**Table 2**  
List of processing experiments carried out for W/O emulsions stabilized by surfactants, biopolymers or particles.

Type	Shear Rate		Frequency sweep		Temperature sweep		References
	Variables	Rate ( $s^{-1}$ )	Temperature (°C)	Parameters tested <sup>a</sup>	Frequency (Hz)	Temperature range (°C)	
<b>Surfactants</b>	Surfactant concentration	0.1–500	50	Viscoelastic region	0.1–100 (at 1% strain)		Almeida et al. (2017)
<b>Surfactants &amp; Biopolymers</b>	Water volume fraction	0.1–1000	25	Viscoelastic region	0.01–50 (at 1% strain)	30–90 (at frequency of 1 Hz and of 1% strain)	Iqbal et al. (2012, 2013a); Wardhono et al. (2014)
	Biopolymer types	0.1–500	25	Viscoelastic region	0.01–100 (at 1% strain)	25–90 (at frequency of 1 Hz and 1% strain)	Iqbal et al. (2013b); Iqbal, et al. (2019a, 2019b)
<b>Particles</b>	Surfactant concentration	1.1–500	25				Massel et al. (2015)
	Particle concentration	100	15				Ahuja et al. (2018)
	Stability of emulsions, microgel concentration, water volume fraction	0.1	25				Zembyla et al., (2020)
	Stability of emulsions	0.1–1000	20	Viscoelastic region	0.1–10 (at 0.05% strain)		Gould et al. (2016)
Surfactant concentration (at constant conc. of particles)	1–100	20				Nesterenko et al. (2014)	
				Water volume fractions	0.1–100 (at 1% strain)		Zhai et al. (2019)
				Particles types	0.01–100		Fernandes et al. (2018)

<sup>a</sup> = In Pickering emulsions, these were the variables tested.

milk and sauces) to 'hard' solids (e.g., butter, margarine, chocolate) (McClements, 2015). Table 2 shows a summary of rheological experiments (shear rate scan, frequency sweep and temperature scan) for W/O emulsions stabilized by low molecular weight surfactants, biopolymers or particles, mainly focusing on gelling the continuous phase or the aqueous phase to enhance the resultant viscosity of the emulsions.

### 6.1. Surfactants

Rheological studies on W/O emulsions stabilized by surfactants (Span 80) generally showed that W/O emulsions have non-Newtonian shear-thinning behaviour with dynamic viscosities ( $\eta$ ) much higher ( $\sim 1$ – $8$  Pa s) than the continuous oil phase ( $\sim 0.14$  Pa s) (Almeida, Charin, Nele, & Tavares, 2017). It was reported that by increasing the surfactant concentration (0.25–3 wt%) in the continuous phase, the bulk emulsion viscosity was increased (from 1 to 8 Pa s, respectively), attributed to free, non-adsorbed surfactant molecules acting as oil-structuring agents (Almeida et al., 2017). In addition, for oil-structured systems, emulsion viscoelasticity properties generally followed a trend such that  $G' > G''$  (measured at 1 Hz and 1 Pa maximum shear stress), indicating that more energy is stored than dissipated, i.e., such emulsions were predominantly elastic.

### 6.2. Biopolymers

Besides altering the rheology of the continuous phase, the  $\eta$  of the aqueous phase can be increased by adding biopolymers, such as proteins or polysaccharides (see 5.2). Massel et al. (2015) showed that addition of pectin to PGPR emulsions gave a significant improvement in stability, whilst  $\eta$  of the whole emulsion system increased from just 0.14–0.22 Pa s, so that the improvement was due to the change in the interior of the droplets or the interfacial film.

Temperature is another important parameter that can be used to control the stability and rheological properties of W/O emulsions (see Table 2). PGPR-stabilized emulsions containing three different types of polysaccharides (pectin,  $\kappa$ -carrageenan or starch) in the aqueous phase (pH 3.5) showed different gelation properties before and after heating (Iqbal, Xu, Huang, & Chen, 2019b). Such behaviour can be attributed to the thermal treatment increasing the thickening and gelling properties of polysaccharides in the droplet phase. Similar results were observed by Iqbal et al. (2012) and Iqbal, Hameed, Baloch, and McClements (2013a), who identified that emulsions containing PGPR in the oil phase and WPI in the aqueous phase showed a more solid-like behaviour at low shear rates and a more fluid-like behaviour at high shear rates, using a temperature treatment from 30 to 90 °C.

Wardhono, Zafimahova-Ratisbonne, Lanoiselle, Saleh, & Clause (2014) measured the viscosity of W/O emulsions at different water volume fractions ( $\phi = 60$ – $80$  vol%) stabilized by PGPR with carboxymethyl cellulose (CMC) and glycerol dissolved in the aqueous phase. All the samples showed shear-thinning behaviour (at shear rates 0.1 to 1000  $s^{-1}$ ) and the initial viscosity (at 0.1  $s^{-1}$ ) increased as the water volume fraction increased:  $\eta$  at  $\phi = 60$  and 80 vol% was 10 and 10<sup>4</sup> Pa s, respectively (Wardhono, Zafimahova-Ratisbonne, Lanoiselle, Saleh, & Clause, 2014). The high values of  $\eta$  at  $\phi = 80$  vol% were due to droplet flocculation but as the shear rate increased the flocs were increasingly disrupted.

### 6.3. Particles

Maia Filho, Ramalho, Lucas, and Lucas (2012) prepared stable emulsions which exhibited predominantly elastic character. Similar results were observed in W/O systems stabilized by silica particles and surfactants (Span 80) (Nesterenko et al., 2014). Silica particles alone in W/O emulsions behaved like an oil thickening agent due to the formation of a three-dimensional network in the oil continuous phase, with  $\eta \approx 8$  Pa s (1  $s^{-1}$ ). However, addition of Span 80 (up to 0.1 wt%) in the



bulk phase caused a further increase in  $\eta$  (to 10 Pa s at a shear rate of  $1 \text{ s}^{-1}$ ) due to adsorption of surfactant to the particle surface. All samples showed shear-thinning as the shear rate increased from 1 to  $100 \text{ s}^{-1}$  and the droplets became increasingly separated from each other, though no coalescence or phase separation was observed.

Zembyla et al. (2020) measured the stability of polyphenol crystal stabilized W/O emulsions (in the presence or absence of WPI or WPM particles in the aqueous phase), as a function of temperature (25, 35 and  $50 \text{ }^\circ\text{C}$ ), using a shear rate cycle between  $10^{-1}$  to  $10^2 \text{ s}^{-1}$  to highlight any shear- and time-dependent hysteresis of  $\eta$ . It was identified that the emulsions stabilized by polyphenol crystals alone, i.e., without WPI or WPM in the aqueous phase, exhibited coalescence after shearing, with the size of the water droplets increasing significantly ( $D_{3,2}$  from  $\sim 7$  to  $\sim 20 \text{ }\mu\text{m}$  for curcumin and from  $\sim 11$  to  $\sim 18 \text{ }\mu\text{m}$  for quercetin). More pronounced destabilization was observed at higher temperatures. The emulsions containing WPI in the dispersed phase were stable to shear and temperature without a significant increase in mean particle size:  $D_{3,2} \approx 19$  and  $11 \text{ }\mu\text{m}$  for both curcumin and quercetin systems, respectively. However, the emulsion system stabilized by polyphenol crystals and WPM particles (in the aqueous phase) showed a very high initial  $\eta$  ( $\sim 10^5 \text{ mPa s}$  at  $10^2 \text{ s}^{-1}$ ) compared to the systems with or without WPI ( $10^3$ – $10^4 \text{ mPa s}$ ). These higher  $\eta$  values were presumably due to flocculation of WPM particles in the continuous oil phase, where the WPM particles seemed to form aggregates with polyphenol crystals, as well as at the interface and also between some water droplets. This appeared to inhibit coalescence under quiescent conditions. However, as noted in the earlier section on polyphenol crystals, even when these aggregates were disrupted by shear and the apparent viscosity was significantly reduced, the emulsions remained stable.

In summary, the rheology of W/O emulsions can be modified by the presence of free (non-adsorbed) surfactant molecules or particles in the continuous phase, which can in turn affect the stability of the droplets. Gelling or increasing the viscosity of the aqueous phase of the droplets, for example by adding biopolymers alongside suitable processing conditions (temperature, pH, etc.), can also lead to modifications that affect emulsion stability, but the emulsion rheology itself to a lesser extent.

## 7. Conclusions

There is considerable emphasis on the development of food products with reduced levels of saturated, trans-fats and total fat, in order to prevent the global increase of obesity and food-linked cardiovascular diseases. This is challenging because of the important role fats have in determining the desirable textural and sensory properties of many food products. Incorporation of water into the fatty phase in the form of water-in-oil (W/O) emulsions may be one strategy to help meet this challenge and this review has summarised how such emulsions might be best provided. There needs to be a clear focus on interfacial design, probably using combinations of surfactants, biopolymers and/or particles to achieve the necessary stabilization via ‘clean-label’ ingredients. More work is required developing biocompatible particles, for example based on cellulose, starch, proteins and organic crystals such as polyphenols. Although most effort has so far been directed at improving W/O emulsion stability, it is crucial that future studies also investigate the oral rheology, tribology and sensory properties of such systems. This is a key missing link that needs to be unlocked before the fundamental colloid science expertise in designing stable W/O emulsion droplets can be translated to real-life food applications for fat reduction purposes.

## Declaration of competing interest

The authors declare no competing financial interests.

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