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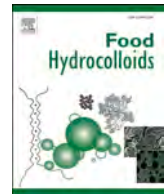
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## Recent advances in design and stability of double emulsions: Trends in Pickering stabilization

Elizabeth Tenorio-Garcia<sup>a</sup>, Andrea Araiza-Calahorra<sup>a</sup>, Elena Simone<sup>b</sup>, Anwesha Sarkar<sup>a,\*</sup>

<sup>a</sup> Food Colloids and Processing Group, School of Food Science and Nutrition, University of Leeds, Leeds, LS2 9JT, UK

<sup>b</sup> Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino, 10129, Italy

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### ABSTRACT

There is an increased pressure on food manufacturers to design low calorie and low fat foods to address the global obesity crisis. Designing double emulsions (DEs) is a microstructural approach to incorporate water that appears as promising fat replacement strategy. However, these complex microstructures are thermodynamically unstable and a thorough understanding of the factors that determine the stability of DEs are required to tailor their functionality. This review provides an update on the main strategies used to stabilize DEs, focusing on the developments in the last five years. Emphasis is placed on the recent use of surfactants, combination of surfactants with gelling agents, particles, fat crystals, and/or coatings. Novel processing techniques were also reviewed, and one-step processing methodologies were particularly examined. We also briefly reviewed the rheological and tribological performance of DEs. Properties and stability of the DEs depend strongly on the formulation and fabrication technique (homogenization, phase inversion, microfluidics, 3D Printing etc). Fat crystal forming a shell around the droplets offers a promising strategy to prevent diffusion of the internal phase in DEs. Pickering stabilization has captured significant research attention, though DEs fabricated solely using particle-laden interfaces are limited. A combined approach of Pickering and bulk stabilization by gelling the aqueous phase appears as a promising strategy to improve stability of DE, which needs research attention. Future studies should focus on characterizing rheological and tribological performance of DEs and link them with mouthfeel perception to accelerate their use in food applications.

### 1. Introduction

Obesity, generally caused by increased energy intake of calorie dense foods, is a leading cause of global health concern nowadays because of its rising prevalence worldwide and associated morbidity and mortality consequences. In fact, more than 1.9 billion adults in the world have excess body weight (WHO, 2020). Not only does excess of body weight promotes chronic conditions such as diabetes, hypertension and cardiovascular diseases and premature death, but it also contributes to the increment of healthcare budget, hospitalization, low work productivity *etc.*, which significantly contributes to the global economic burden (Anekwe *et al.*, 2020).

Among many strategies used to address obesity, reformulation approaches, for instance, attempt to enhance consumers diet by reducing calories in industrially-produced food products. The reformulation model plan of the Organisation for Economic Co-operation and Development (OECD) forecasts that a reduction of 20% of calories in high

sugar, salt, calories and saturated fat products could avoid up to 1.1 million cases per year of cardiovascular diseases, diabetes and cancer by 2024 (Shekar & Barry, 2019). Consequently, identifying appropriate ingredients or technologies to replace the most calorie-intense food products, *i.e.* fat based ones, is one of the promising strategies used by food manufacturers to respond to consumers' demands and growing pressures from food regulatory bodies. Hence, there has been strong research focus in the colloid science community to design new fat replacers (Kew *et al.*, 2020). When using fat replacers, it is important that the final products render similar characteristics to whole-fat food such as microstructure, physicochemical and sensorial characteristics, which to a large extent, depend on fat content, type and colloidal structure (Carcelli *et al.*, 2020; Xingyun & Yuan, 2017). In fact, different type of microstructures can be used to mimic fat properties, such as droplets, bubbles (Metilli, Lazidis, *et al.*, 2021; Metilli, Storm, *et al.*, 2021).

A microstructural change can confer different texture to a food product. For instance, yoghurt obtains its textural properties such as

\* Corresponding author.

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

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firmness attributes and mouthfeel attributes (e.g., creaminess and smoothness) from its emulsion-filled gel structure (i.e. fat droplets that are dispersed within a proteinaceous gel matrix) (Liu et al., 2015). On the other hand, textural properties of ice cream are attributed to the air bubbles that are stabilized by partially coalesced fat crystals by so-called Pickering stabilization (Fredrick et al., 2010). Also, the polymorphic properties of fat crystals are crucial for the sensory properties of chocolate and its storage stability (Ewens et al., 2021; Patel & Dewettinck, 2015). Therefore, a thorough understanding of the structure and functionality of colloidal components in whole-fat product is required to design fat reduction strategies.

One of the key approaches to incorporate large proportions of non-caloric water to replace calorie-dense fat has been to design multiple emulsions. The most common multiple emulsions are double emulsions (DEs), which are compartmentalized systems in which the dispersed droplets of simple emulsions contain smaller oil-in-water (O/W) or water-in-oil (W/O) droplets within them. The advantages of DEs over simple emulsions are the capability of the former to simultaneously encapsulate and release different hydrophilic and/or lipophilic components and to provide substantial fat reduction with having two aqueous phases (Jiménez-Colmenero, 2013; Xiao-Wei et al., 2019). The most common types of DEs are water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) emulsions (Dickinson, 2015).

The foremost applications of W/O/W emulsions are to encapsulate sensitive components, such as vitamins, antioxidants, and microorganisms, among others (Eslami et al., 2017; Liu, Kharat, et al., 2020). More recently, they have been used to further reduce the fat content of O/W emulsion-based products and thus are considered as an effective strategy to engineer low-fat products (Oppermann et al., 2016; Pawlik & Norton, 2014; Rebry et al., 2020), whilst, maintaining or even enhancing the perception of fat-related sensory attributes such as creaminess, fattiness, cohesiveness and thickness (Oppermann et al., 2016). Meanwhile, O/W/O emulsions have been used to add flavouring ingredients to increase taste perception in fat continuous products, such as margarine (Eisinaite et al., 2017; Kesatoshi et al., 1990; Masanori et al., 2012; Muschollik & Dickinson, 2017). Furthermore, according to Oppermann et al. (2016), a fat reduction of up to 47% can be achieved in multiple emulsions when the inner water phase is gelled with biopolymers (Oppermann et al., 2016). Less common types of DEs are oil-in-oil-in-water (O/O/W) emulsions, which allows incorporating poorly soluble actives in both water and oil (when the actives are soluble in polar organic solvents) (Wang et al., 2017). Other exotic possibilities are water-in-water-in-water (W/W/W) or water-in-water-in-oil (W/W/O) emulsions, which require the presence of two immiscible aqueous phases (e.g. dextran and polyethylene glycol solutions) (Cui et al., 2017), air-in-oil-in-water (A/O/W) (Goibier et al., 2019) or even more complex morphologies such as triple emulsion i.e. W/O/W/O, O/W/O/W and W/O/O/W (Nabata et al., 2021) or quadruple emulsions i.e. W/O/W/O/W or O/W/O/W/O (Silva et al., 2016). Although in principle, triple and quadruple emulsions can protect several sensitive substances, they have been rarely studied in literature. For instance, Xiao-Wei et al. (2019) have co-encapsulated multiple photosensitive components in a triple  $W_2/O_2/(O_1/W_1)$  emulsion using polyglycerol polyricinoleate (PGPR) and quillaja saponin surfactants in a three stage process (Xiao-Wei et al., 2019).

For stabilization of DEs, two different surfactants are generally needed. For instance, to stabilize the inner interface in a W/O/W emulsions, a hydrophobic surfactant with a low hydrophilic-lipophilic balance (HLB) value (smaller than 7) is needed. Meanwhile, for the external interface (O/W), a hydrophilic surfactant with a high HLB value (greater than 12) is added (Ding et al., 2019). However, surfactant-stabilized DEs do not provide enough thermodynamic stability against coalescence, Ostwald ripening and flocculation. In DEs, the multiphase system allows additional mechanisms of destabilization such as diffusion of the inner phase and the outer phase due to gradient in osmotic and Laplace pressure, plus the coalescence of the inner

droplets. Thus, to overcome these destabilization issues in DEs, solid particles have recently emerged as a potential solution to provide ultrastability to DEs (Olusanya & Binks, 2020; Ruan et al., 2018). When partially wetted by the phases, particles offer more stability against coalescence and Ostwald ripening when compared to surfactant-stabilized DEs. This is because of the high desorption energy (several thousands of  $k_B T$ , where  $k_B$  is Boltzman constant and T is temperature) that is required to remove the adsorbed particles from the liquid-liquid interface in Pickering emulsions as compared to considerably lower values (5–10  $k_B T$ ) typical of surfactants, latter tend to reversibly attach at the interface (Berton-Carabin & Schroën, 2015; Sarkar & Dickinson, 2020).

Recent research work on DEs has mainly focused on the use of surfactants at both interfaces, a combination of surfactants and gelling agents to gel either the water phase or crystallize the fat phase, or the use of Pickering particles to stabilize either the inner or the outer emulsion, to enhance DE stability during processing and storage (Balcaen et al., 2021; Chiu et al., 2017; Fernandez-Martin et al., 2017; Flaiz et al., 2016; Herzi & Essafi, 2018, 2019; Jiang et al., 2021; Klojdova et al., 2018; Lin et al., 2020; Liu, Kharat, et al., 2020; Nelis, Declerck, et al., 2019; Pritchapan et al., 2021; Silva et al., 2018; Spyropoulos et al., 2019; Tian et al., 2021; Wang et al., 2018; Xiao et al., 2017; Xing et al., 2018). However, a few studies have focused on the use of only the Pickering stabilization mechanism for both the O/W or W/O interfaces of the DEs (Olusanya & Binks, 2020; Ruan et al., 2018; Spyropoulos et al., 2019).

For understanding the features of surfactant-stabilized DEs, their processing methods and applications, we recommend readers to the literature reviews by Muschollik and Dickinson (2017), Jiménez-Colmenero (2013) and Ding et al. (2019), which serve as elegant pre-reads for this review. However, to the best of our knowledge, there is no recent literature review that focuses on Pickering stabilization of DE by food grade particles and/or fat crystals. More importantly, the textural and mouthfeel properties of DEs have attracted rare attention; nevertheless these are crucial for the applications of DEs as fat replacers. In addition, the advent of additive manufacturing (AM) i.e. 3D printing has also led to significant development in fabrication of DEs, which needs to be discussed.

Therefore, the aim of this literature review is to provide a thorough understanding of DEs with a special focus on the ones stabilized by food-grade Pickering particles that have been studied in the last five years. It has been recently demonstrated that fat crystals provide stabilization of DEs by various mechanisms such as Pickering stabilization as well as forming a shelled structure around the water droplets, thus, the properties and influence of fat crystals in DE stability are examined. In the first part of this review, an overview of DE processing is covered. However, since emulsification methods for the fabrication of DE have been already extensively reviewed, we have particularly focused on the novel methodologies used in the last five years for processing, such as phase inversion with a single stabilizer. Then, a discussion on various ingredients and strategies to reach thermodynamic stability of DEs is covered, with a particular emphasis on food grade particle-laden interfaces. In this review, we only focus on W/O/W emulsions, as these are commonly used for fat replacement purposes. The examination of the rheological and tribological properties of DE in the context of the application of DE as fat replacers is discussed. And, finally, we provide future perspectives on DEs intended for fat replacement applications. The literature search was conducted using three key search engines: Science Direct, Web of Science and PubMed and we also included a patent scan of the last five years. Table 1 lists all the abbreviations that have been used in this review.

## 2. Novel emulsification processing techniques for DEs

A range of processing techniques are used to prepare DEs with the most conventional being a two-step process (Fig. 1a) followed by new techniques such as the one step-phase inversion process (Fig. 1b) and

**Table 1**  
Abbreviations used in the paper.

AM	Additive manufacturing
AMF	Anhydrous milk fat
A/O/W	Air-in-oil-in-water
CB	Cocoa butter
CHI	Chitosan
CMC	Carboxymethyl cellulose
CMCC	Colloidal microcrystalline cellulose
CO	Coconut oil
CP-CaP	Corn-peptide-decorated calcium phosphate particles
Cryo-SEM	Cryogenic-scanning electron microscopy
DEs	Double emulsions
DPEs	Double Pickering emulsions
DSC	Differential Scanning Calorimetry
EC	Ethylcellulose
EE	Encapsulation efficiency
EGCG	catechin (–)-epigallocatechin-3-gallate
ETPTA	Ethoxylated trimethylolpropane triacrylate
G'	Storage modulus
G''	Loss modulus
GA	Gum Arabic
GDEs	Gelled double emulsions
GMS	Glycerol monostearate
GNP	Gliadin nanoparticles
GS	Glyceryl stearate
Hap	Hydroxyapatite
HLB	Hydrophilic–lipophilic balance
HPH	High pressure homogenizer
HPMC	Hydroxypropyl methyl cellulose
HOSOFO	High oleic sunflower oil
HSO	Hydrogenated soybean oil
HTy	Hydroxytyrosol
IPM	Isopropyl myristate
JH	Jet homogenizer
LBG	Locust bean gum
LCT	Long chain triglyceride
LP	Liquid paraffin
MAGs	Monoacylglycerols
MCT	Medium-chain triglyceride
MS	Magnetic stirring
NaCas	Sodium caseinate
NMR	Nuclear Magnetic Resonance
OECD	Organisation for Economic Co-operation and Development
OSA	Octenyl succinic anhydride
OSQS	OSA-modified quinoa starch
O/W	Oil-in-water
O/W/O	Oil-in-water-in-oil
PC	Phosphatidyl choline
PFM-NMR	Pulse field gradient nuclear magnetic resonance
PGPR	Polyglycerol polyricinoleate
PHSO	Hydrogenated sunflower oil
PIT	Phase inversion temperature
PMMA	Polymethyl methacrylate
RBO	Rice bran oil
RH	Rutin hydrate
RSB	Rotor stator blender
SA	Saponin
SDR	Spinning disc reactor
SFC	Solid fat content
SFO	Sunflower oil
sPMF	Soft palm mid fraction
SO	Soybean oil
SSL	Sodium stearoyl lactylate
TAG	Triacylglycerol
TGCR	Tetra glycerin condensation ricinoleate
W <sub>1</sub>	Dispersed aqueous phase in a W/O/W DE
W <sub>2</sub>	Continuous aqueous phase in a W/O/W DE
W/O	Water-in-oil
W/O/W	Water-in-oil-in-water
WPI	Whey protein isolate
W/W/W	Water-in-water-in-water
XG	Xanthan gum
YP	Yellow pigment

microfluidic techniques (Fig. 1c).

### 2.1. Two-step process

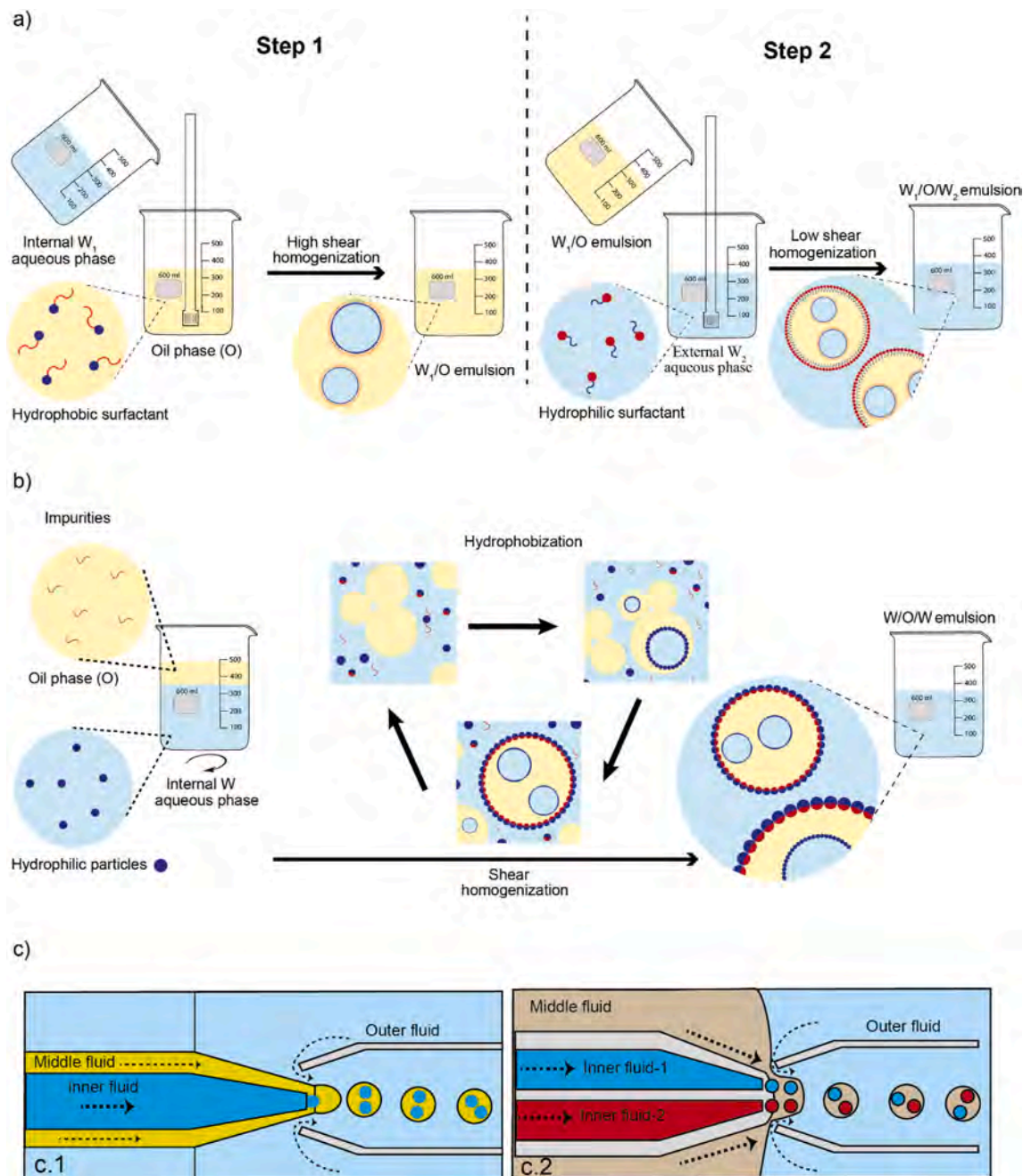
Briefly, in the two steps process (Fig. 1a), a surfactant with a low HLB value is added firstly to the continuous phase (O) and then it is subjected to high shear forces with the dispersed phase (W<sub>1</sub>) forming a simple W/O emulsion. In the second stage, a surfactant with a high HLB value is added to the external aqueous phase (W<sub>2</sub>) and a second homogenization takes place at a lower shear rate to form the DE (Flaiz et al., 2016; Silva et al., 2018; Sun et al., 2019). For an O/W/O emulsion, the same process is applied but using an emulsifier with high HLB values in the first stage and then surfactant with low HLB value in the second stage.

The second step in the formation of DEs is crucial to determine their final microstructure. Stronger mechanical force are required in this step to incorporate the previously formed water-in-oil emulsion droplets into the dispersed aqueous phase, and therefore a simple O/W simple emulsion is obtained, latter contains W/O emulsion droplets (Ruan et al., 2018). Fig. 2 shows unpublished work done in our laboratory where different devices have been used in the second stage to examine the difference in the microstructures of the DEs obtained. Such devices include: spinning disc reactor (SDR), rotor stator blender (RSB), magnetic stirring (MS), high-pressure homogenizer (HPH) and the combination of magnetic stirrer and high-pressure homogenizer (MS/HPH). As each method has its own working principle (Fig. 2a), the final microstructure of emulsions generated is different and such second stage processing may result in the formation of a simple or a double emulsion (Fig. 2b). For instance, HPH forms emulsions by the application of very high turbulence and shear rate, generated when the dispersed phase passes through the hole into the homogenization chamber by the applied pressure (Burgaud et al., 1990). The high-energy produces small droplets when the aqueous phase impact with the homogenizing chamber walls (Fig. 2a). On the other hand, in the SDR, the fluid (in this case the blend of the dispersed (W<sub>1</sub>/O) and continues phase W<sub>2</sub>) enters the top of a disc that is rotating at a high speed; thus, the emulsification process is associated with the force generated by the disc's velocity. This high rotating speed causes the fluid to be expelled. During this process, ligaments are formed around the disk rim and finally fragmented into droplets (Fig. 2a) (Wang et al., 2016). In the SDR, the fluid is transported to the top of the disc by a continuous flow for several minutes in contrast to few seconds in the case of HPH. In HPH, strong forces allow the oil phase (O), which contain the water droplets (W<sub>1</sub>) of the primary emulsions, to act as the dispersed phase with the continuous aqueous phase (W<sub>2</sub>) forming the second emulsion (Fig. 2b).

Despite two-step processes are the most commonly applied technique to produce DE, their implementation in the food industry is not straightforward because of the multiple unit operations involved and potential issues with upscaling (Muscholik & Dickinson, 2017). Besides, the energy applied in the second step can lead to destabilization of the DEs (Ruan et al., 2018). Thus, one-step methodologies are surfacing the literature recently. In particular, phase inversion and microfluidics seem to be promising alternatives to address these processing issues caused by the two step conventional processes.

### 2.2. Incomplete phase inversion

Phase inversion is commonly used in industry to reverse simple emulsions (for example, O/W to W/O) because of the low energy input required, the monodisperse distribution of the droplets and their small size (lower than 1 μm) obtained. Phase inversion simplifies the manufacturing process as the simple emulsion formation happens by interfacial properties, such as interfacial tension, viscoelastic behaviour of the interface and hydrodynamic fields in the break-up and re-coalescence emulsification process, in one single step (Lucassen-Reynders & Kuijpers, 1992; Wang et al., 2018). The method is based on the curvature properties of surfactants and their dependence to external parameters,



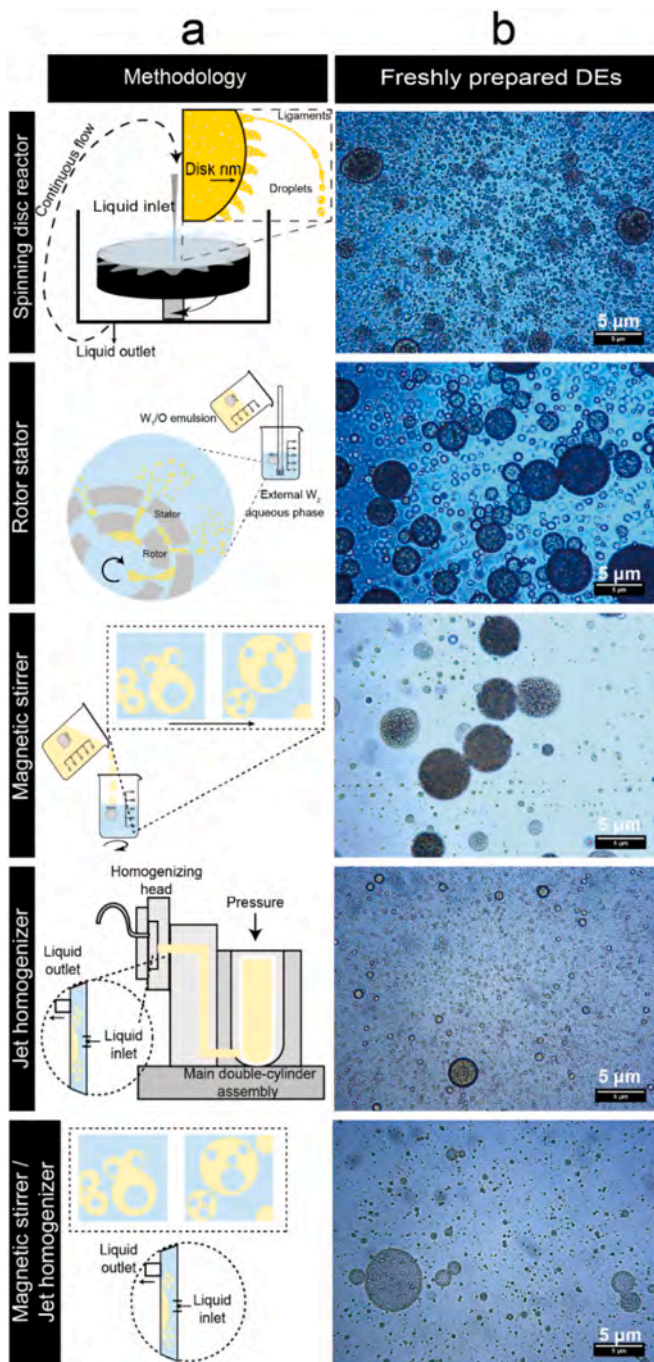
**Fig. 1.** Schematic presentation of different methodologies used to prepare DEs: a) two-step emulsification used for surfactant-stabilized DE, b) one-step emulsification used for particle-stabilized DEs and c) microfluidic device used to prepare DEs (1) and DEs with different composition in the inner aqueous phase (2). Figure c) adapted from Adams et al. (2012).

such as temperature, pH, ionic strength, degree of saturation of the oil, and the presence of a co-surfactants (Leal-Calderon et al., 2007). The temperature, for instance, can modify the surfactant head groups altering their hydration properties, this methodology is known as phase inversion temperature (PIT). During phase inversion, a DE can be formed by stopping the process at an intermediate stage. This DE is the result of the collision of multiple droplets, which drives the enclosing of the draining film of the bulk phase to the coalesced droplets (Fig. 1b). The interruption of the inversion is achieved by the appropriate use of stabilizers, mainly amphiphilic molecules, and the presence of other components that modify the polarity of the stabilisers themselves (Kim et al., 2018).

The stabilizers used to prevent the complete inversion of the emulsion must allow the coalescence of the outer droplets, so that the inner

droplets can be entrapped. But the inner droplets must be sufficiently stable and to enable their interaction enable the formation of the DEs (Kim et al., 2018). For instance, a stable O/W/O DE was achieved by using silica nanoparticles to stabilize the secondary emulsion (W/O), while polymethyl methacrylate (PMMA) was used for the primary emulsion (O/W). In this system, it was demonstrated that the presence and the concentration of the PMMA were crucial in order to stabilize the inner oil droplets and modify the surface of the silica particles. It was observed that, at the end of the inversion process, the water droplets reached their stability by the absorption of PMMA at the silica-stabilized interface (Kim et al., 2018).

The chemical composition of the oil has also been observed to be crucial in the formation of a DE in the one step process when either surfactant or particles are used to stabilize the interfaces. For instance,



**Fig. 2.** Second-step processing techniques used to prepare a W/O/W DE (a) and their microstructure after preparation (b) obtained using optical microscopy. These DEs are prepared at the Laboratory of Food Colloids and Bioprocessing, School of Food Science and Nutrition University of Leeds (unpublished work). The primary O/Ws were prepared using PGPR (7.0 wt%) and WPI (3.0 wt%).

when preparing W/O/W DEs using a combination of Span 85 and Tween 80 as surfactants, and three different types of oils, medium-chain triglycerides (MCT), isopropyl myristate oils (IPM) and liquid paraffin (LP), DEs were only formed with MCT and IPM (Wang et al., 2018). The result was explained to be due to the relationship between high water-oil interfacial tension ( $49.43 \pm 0.69$  mN/m) and the poor polarity of the oil. Similarly, the stabilization of both interfaces of a Pickering DEs with corn-peptide-decorated calcium phosphate particles (CP-CaP) was improved when algal oil was added to sunflower oil. This was explained by the fact that the three-phase contact angles of the particles increased

proportionally to the ratio increment of the algal oil, being  $80.0 \pm 19^\circ$  in pure sunflower oil and  $130 \pm 2.8^\circ$  for pure algal oil. Meanwhile, when the algal oil was purified with Florisil to remove free fatty acids, the contact angle was reduced to  $74.9 \pm 2.5^\circ$ . The significant difference between the three-phase angles was explained by the capability of the polyunsaturated fatty acid to enhance the adsorption of the CP-CaP particles at interfaces. As a result, DEs were not formed with sunflower oil and purified algal oil as the oil phase. In addition, the presence of free fatty acids in algal oil modified the surface of the CP-CaP particles allowing their hydrophobization, and therefore, the stabilization of the oil-water interface. Thus, it was concluded that the CP-CaP particles can stabilize both W/O and O/W emulsions, by the existence of CP-CaP and hydrophobized CP-CaP particles during the emulsification process forming W/O/W DEs (Ruan et al., 2018). However, there are limited types of particles that can act as stabilisers of both interfaces (Hong et al., 2012; Tu & Lee, 2012) and that are also suitable for human consumption (Ruan et al., 2018).

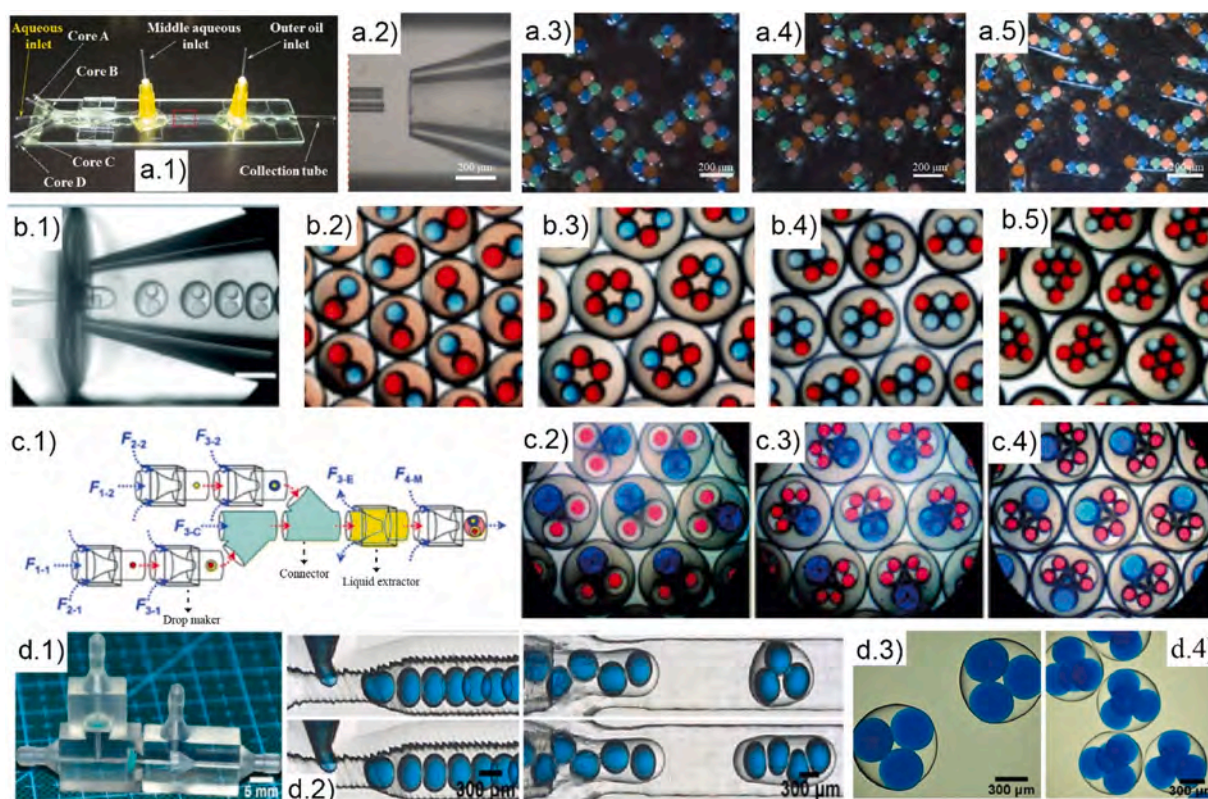
### 2.3. Microfluidic strategies

Microfluidic strategies use devices with microchannels units that can easily create simple or multiple emulsion depending on the assembled geometry (Fig. 1c). Various devices used to create DEs using microfluidics are shown in Fig. 3a–d. The components of the DEs pass through different concentric microchannels that allows the formation of drops with the inner and the middle fluid, while these are put into the outer fluid. Microfluidic devices possess some attractive advantages over the two-step emulsification processes (Fig. 1a). For instance, DEs containing monodisperse populations of both the inner and the outer droplets with a coefficient of variation lower than 5% can be obtained. Besides, microfluidics allow the encapsulation of 100% of the bioactive components dissolved in the dispersed phases (Silva et al., 2016). Finally, microfluidic devices allow adapting stages to produce higher-order multiple emulsions (triple and quadruple emulsions) with controlled droplet sizes (Fig. 1c).

Another interesting value is that the composition of the inner droplets in DEs can be varied. For example, Zhao, et al. (2012) used a capillary device (Fig. 3a1 and 3a2) to create O/W/O DEs with three or four different inner phases using multiple photonic crystals or magnetic-tagged ETPTA (ethoxylated trimethylolpropane triacrylate) cores (Fig. 3a3 and 3a4). The authors also produced DEs with rod-like (Fig. 3a5) droplets by adapting the multiple injections tubes (cores A-C Fig. 3a1) at different distances. This variability in the inner phases provide interesting biomedical applications such as 3D scaffolds for tissue regeneration and increase the sensitivity of particle-based assays by the presence of magnetic elements (Zhao et al., 2012).

In addition, the number and composition of the inner droplets can be controlled in a W/O/W DEs (Fig. 3b1 and 3b2). Microfluidics device can control accurately the quantity of different types of inner droplets by modulating the flow of the different fluids (Fig. 3b3, 3b4 and 3b5) (Adams et al., 2012). For example, O/W/O/W triple emulsions were made with controlled number, composition and size of the inner droplets by assembling additional building blocks (see Fig. 3c1) to the basic microfluidic device formed by a liquid extractor, connector and drop maker. This can be seen in Fig. 3c2, 3c3 and 3c4 (Wang et al., 2011). It is worth noting that microfluidics technology is far from being used in food products because of the high cost, upscaling issues and limited production efficiency (Vladisavljević et al., 2017). Nevertheless, microfluidics could still be useful for the manufacturing of premium food products requiring encapsulation of flavourings and bioactives using food grade emulsifiers.

3D Printing, also known as additive manufacturing (AM), has been used to manufacture more economically affordable microfluidic equipment (Fig. 3d1 and 3d2) to manufacture triple and quadruple DEs (Fig. 3d3 and 3d4). Nevertheless, there are still some challenges to tackle. Some of the current drawbacks are 1) material biocompatibility,



**Fig. 3.** Microfluidics devices used to produce double and higher-order emulsions. a) Capillary device and micrographs of microfluidics device used to produce O/W/O DEs (a.1), micrograph of the internal structure of the device (a.2), O/W/O DEs with three and four different photonic crystal cores in the inner droplets (a.3 to a.4) and rod-like photonic crystal DEs (a.5) (Zhao et al., 2012). Inner design of the microfluidic device used to fabricate W/O/W DEs (b.1) and the micrographs of DEs with two different composition of the inner droplets containing different number of inner droplets (b.2 to b.5) (Adams et al., 2012). Drawing of a microfluidic device use to create high-order DEs (c.1) and the micrographs of the O/W/O/W triple emulsions with different composition of the inner droplets (c.2 to c.3) and novel triple emulsions containing one simple emulsion and two DEs (c.4) (Wang et al., 2011). Printing microfluidics device (d.1) and micrographs of the inner structure in the printing device and micrographs of DEs obtained with different number of inner droplets (d.2) i.e. three (d.3) or four (d.4) droplets (Zhang et al., 2019). Reproduced and adapted with permissions from PNG Asian Materials (images a.1 to a.5), Royal Society of Chemistry (images b.1 to b.4 and c.1 to c.4), and Nature (image d.1 to d.4).

as traces of glass cannot be detected, a 3D printed device might leak toxic compounds, 2) printed channel quality (Fig. 3c2), which affects the flow of droplets (breaking them) due to uneven surfaces, and 3) the limited dimension of 3D printed channels, which are significantly larger in diameter than for conventional microfluidic devices, and hence produce droplets of bigger sizes. For instance, depending on the printing technique, AM devices have been observed to produce droplets within a range of 100  $\mu\text{m}$ –500  $\mu\text{m}$  (Ji et al., 2018; Zhang et al., 2019) (Fig. 3c3), which is considerable higher compared to microfluidics devices (10  $\mu\text{m}$ ) manufactured using different techniques (Clegg et al., 2016). However, for the food industry, the first step to address should be to investigate the use of food-grade emulsifiers to generate droplets in the microfluidic device and then to consider scaling up of the microfluidic technology (Muijwijk et al., 2016).

### 3. Stabilization mechanisms in double emulsions

The stability of DEs is quite more complex compared to the simple emulsions. Besides the common destabilization mechanisms related to simple emulsions (flocculation, creaming, Ostwald ripening and coalescence), further coalescence processes happens in the inner droplets in DEs. In addition, the presence of two interfaces contribute to the existence of a particular destabilization process of DEs, which involves mass transfer during storage. Osmotic imbalances produce mass flow between the dispersed ( $W_1$ ) and the continuous ( $W_2$ ) aqueous phases of a  $W_1/O/W_2$  emulsion, which allows the diffusion of the aqueous phase and the encapsulated compound outside the droplets. These transport

phenomena could lead to the breakup of the DE and therefore the loss of its functional properties. For instance, the inner water may diffuse into the external water phase (higher osmotic pressure in the external aqueous phase) or vice versa depending on the osmotic pressure gradient, which might cause shrinkage and swelling of the double emulsions, respectively (Ding et al., 2019).

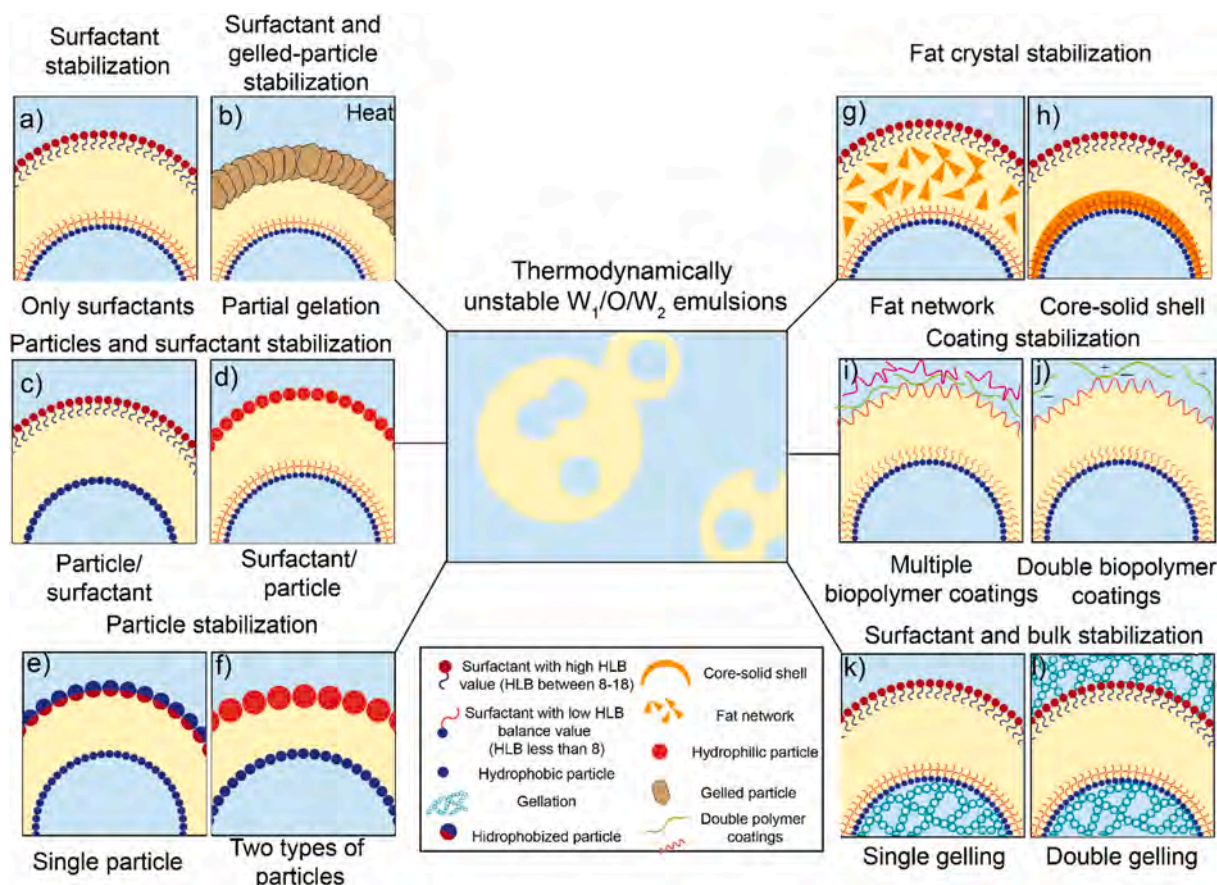
The stability of DEs have been evaluated by measuring the changes of the external droplet size (the oil droplets in a W/O/W emulsion), the evolution of the microstructure of the DEs using microscopy images, visual changes like creaming, the release and encapsulation efficiency (EE) of bioactive compounds or markers and yield efficiency (the amount of water entrapped). The EE of freshly prepared emulsions and the capability of the DE systems to retain the encapsulated compound or marker as a function of storage time are determined by measuring its concentration in the  $W_2$ . Hence, concentration of the bioactive compounds or markers after release have been considered as an indirect indicator of the stability of the emulsions. However, the diffusion mechanism also depend on molecular structure of the encapsulate, thus, the same system of the DEs could present different release degree and kinetics just by changing the structure of the marker. Besides, increase in the encapsulate concentration in the  $W_2$  might also be associated with coalescence of the water droplets  $W_1$  and the continuous phase  $W_2$  (Leister & Karbstein, 2020, 2021). Commonly, the EE and the encapsulate release are measured by spectroscopy or conductivity methods.

Alternatively, differential scanning calorimetry (DSC), analytical photo-centrifugation and low pulse field gradient nuclear magnetic resonance (PFG-NMR) have been used to measure the water content in

DEs as a direct measurement of their stability. Determining the droplet size of the  $W_1$  droplets is relevant as they define the droplet size of the outer droplets ( $O/W_2$ ), for example, the shrinkage or swelling of the oil droplets may affect the structure of the DEs by decreasing or increasing the oil droplet size, respectively. Nevertheless, the main challenge in measuring the stability of DEs, is the measurement of the inner droplets size, and to the best of our knowledge, PFG-NMR and confocal light scattering are the only two methods used to measure this parameter in  $W/O/W$  emulsions. For further information on the methodologies used to evaluate the stability of DEs, the reader could refer to the reviews of [Leister and Karbstein \(2020\)](#) and [Muschiolik and Dickinson \(2017\)](#) and the work of [Nelis, Declerck, et al. \(2019\)](#) and [Nelis, Declerck, et al. \(2019\)](#). For practical purposes, from now on we will call stability against diffusion, the ability to avoid the release of bioactive compounds or the water diffusion, but it is important to take in mind that with this parameter is not possible distinguish between a diffusion phenomenon and the coalescence between the  $W_1$  droplets and to the continuous  $W_2$  phase. To evaluate coalescence, single-droplet methods might be implemented to the characterization of DEs systems ([Leister & Karbstein, 2021](#)). However, the encapsulation efficiency of bioactive molecules is out of the scope of this review. The effect of coalescence of inner droplets on the macroscopic properties of the DEs has not been studied to date. Though the macroscopic properties might be determined by the external droplets ([Leister & Karbstein, 2020](#)), research on the rheological properties of DEs depending on the structure of the inner droplets is relatively rare ([Luo et al., 2017](#)). In the next sections, the different strategies that have been followed to enhance the overall stability in DEs

will be briefly discussed. The information reported here is for  $W/O/W$  emulsions, unless otherwise specified. [Fig. 4a-4l](#) illustrate schematically the structure of DEs stabilized with different strategies using surfactants, fat crystal networks, particles, biopolymers either alone or in combination. Some examples of microstructures of DEs created using surfactants with/without gelling agents ([Fig. 5a-c](#)), particles ([Fig. 5d-f](#)), surfactants and particles ([Fig. 5g-i](#)) and combination of surfactants, particles and/or fat crystals ([Fig. 5j-l](#)) are examined and discussed in this section.

It is evident that most of the research done to date still use surfactants as main stabilizers ([Fig. 4a](#)) with or without the use of biopolymers as gelling agents (see microstructures in [Fig. 5a-c](#)). Particularly, as there has been an enormous development of food-grade particles (lab-synthesized or nature-derived) to stabilize  $W/O$  emulsions in recent years, studies have surfaced that have combined the classical surfactant used for DEs *i.e.* polyglycerol polyricinoleate (PGPR) with hydrophilic or hydrophobic particles (see [Fig. 4b, c](#) and [4d](#) for schematic representation and [Fig. 5g-i](#) for examples of microstructures). However, its worth noting that only a few studies are present to date where DEs are stabilized solely by particles ([Fig. 4e](#) and [f](#)), some examples of such microstructures are shown in [Fig. 5d-f](#) where a range of bio-derived and processed, laboratory synthesized and natural particles without further processing are used. There has also been an upsurge in research interests in using fat crystal network in combination with surfactants to fabricate DEs where sometimes the oil phase is gelled and in other cases, where the fat crystals gel at the interface forming a shelled structure ([Fig. 4g](#) and [h](#), see microstructures in [Fig. 5j-l](#)). Coating the interface using



**Fig. 4.** Different strategies used to stabilize the water/oil interface and the oil/water interface of DEs: a) surfactant/surfactant stabilization, b) surfactant and gelled-particle stabilization, c) particle/surfactant stabilization, d) surfactant/particle stabilization, e) one single particle acting in both phases as stabilizer, f) two different types of particles acting as stabilizers, g) surfactant stabilization combined with fat network stabilization, h) core-solid shell, i) surfactant stabilization/multiple coating stabilization by biopolymers, j) surfactant/double coating stabilization by biopolymers, k) surfactant stabilization combined with single gelling bulk stabilization (external or internal aqueous phase) and l) surfactant with double gelling bulk stabilization (external and internal aqueous phase).



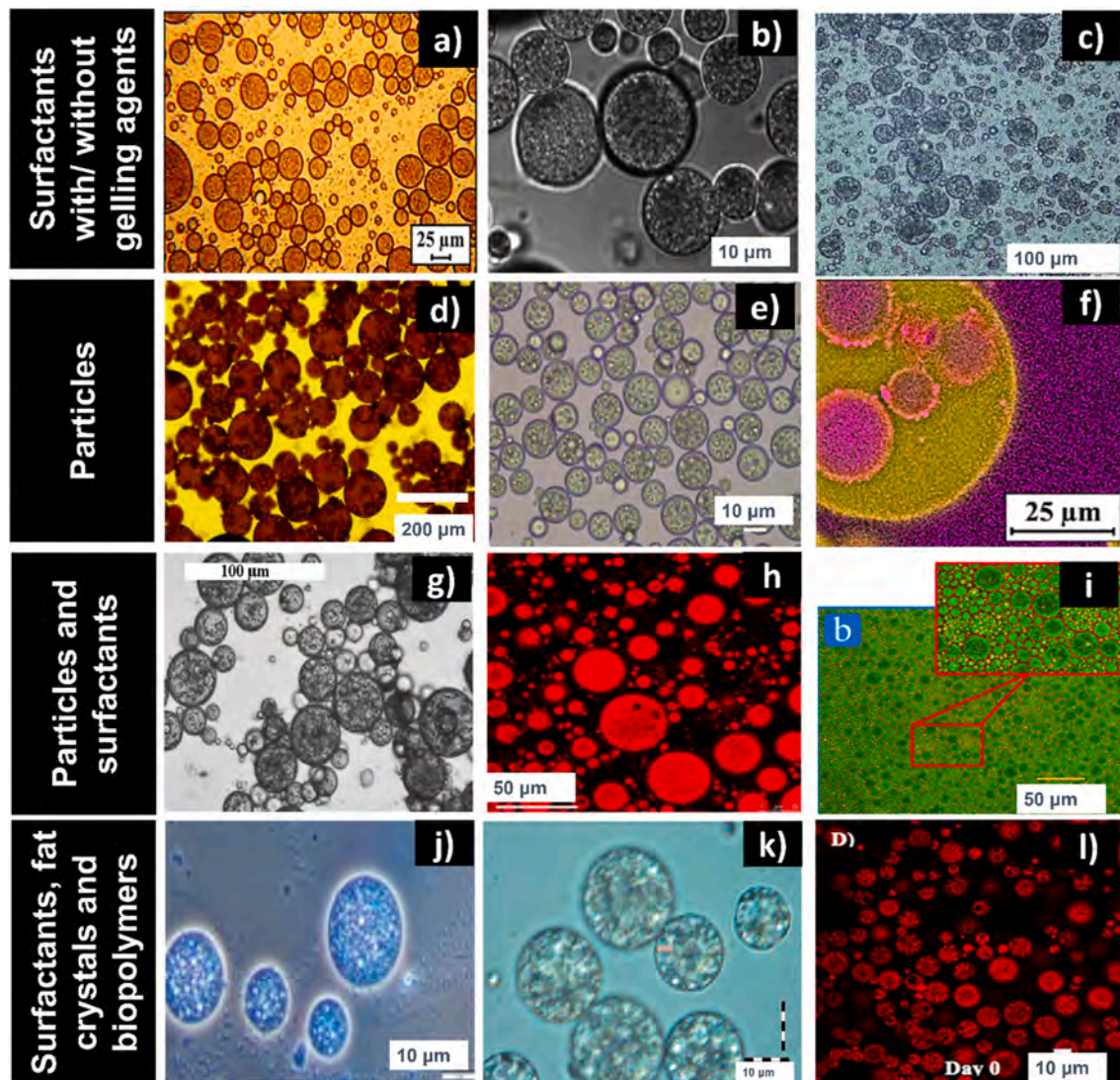


Fig. 5. Micrographs of water-in-oil-in-water emulsions stabilized using different types of stabilizers (surfactant, particles, biopolymers and/or fat crystals), oil phase and/or additional stabilizers and/or gelling agents. a) PGPR/Tween 20 (Spyropoulos et al., 2019), b) WPI (gelling agent  $W_1$ ) PGPR/WPI (Oppermann et al., 2015), c) PGPR/sunflower lecithin/carrageenan (Klojdova et al., 2018), d) Yellow pigment (PY)/Orange pigment (PO) (Olusanya & Binks, 2020), e) Corn-peptide-functionalized calcium phosphate particles (Ruan et al., 2018), f) Ethylcellulose (EC)/Rutin hydrate (RH) (Spyropoulos et al., 2019), g) PGPR/kafirin particles (Xiao et al., 2017), h) PGPR/Octenylsuccinate quinoa starch (OSQS) (Lin et al., 2020), i) Gelatin (gelling agent)/PGPR/Gliadin nanoparticles (Xing et al., 2018), j) Medium chain triglyceride (MCT) (Crystallisable fat)/Glycerol monostearate/PGPR/Tween 80/sodium alginate (Molet-Rodríguez et al., 2021), k) Anhydrous Milkfat (AMF) (Crystallisable fat)/PGPR/Sodium caseinate/Xanthan (thickening) (Herzi & Essafi, 2019), l) hydrogenated soybean oil (HOSO) (crystallisable fat)/PGPR/Quillaja saponin/gum Arabic (Liu, Zhou, et al., 2020). Reproduced with permissions from American Chemical Society (images a, f, i), Elsevier (images b–c, g–h, k–l), MDPI Company (image j), Royal Society of Chemistry (image e), and Taylor & Francis (image d). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

biopolymers (Fig. 4i and j) as well as gelling of one/both of the aqueous phases *i.e.*  $W_1$  and  $W_2$  (Fig. 4k and l) have also been implemented recently to improve the stability of DEs. Tables 2–5 show a non-exhaustive list of formulations used to prepare DEs using various strategies (surfactants, particles, fat networks, biopolymers and combination thereof), their size as well as their stability during storage that have surfaced in the last few years, some of the examples are discussed in the next subsections.

### 3.1. Surfactant stabilization

Surfactants such as PGPR are widely used to stabilize W/O/W DEs (Table 2). Sometimes a combination of surfactants are used (Fig. 4a). However, the use of surfactants at both interfaces might confer additional instability to the system. For instance, using a combination of

PGPR with Tween 20 (Spyropoulos et al., 2019) produces DEs with  $D_{4,3}$  values of  $\sim 25 \mu\text{m}$  (Fig. 5a), however, they tend to destabilize after a week (Table 2) with substantial loss of  $W_1$ . Surfactants have a molecular structures, so they tend to move across the different phases (Neumann et al., 2018). Besides, surfactants can also transport ions either in the dispersed or continuous aqueous phase of a W/O/W emulsion, by three different mechanism: 1) thin lamellae, 2) hydrated surfactant and 3) reverse micelle (Cheng et al., 2007). This allows the transport of water across the interfaces, as ions transport by reverse micelle containing the solvated ions.

The concentration and the type of surfactants chosen to stabilize both interfaces also contribute to the instability of DEs. Leister and Karbstein (2021) corroborated this theory by using a single droplet study in a cuvette. The  $W_1$  droplet was placed at the surface of the oil and  $W_2$  surface separately, containing the low and the high HLB surfactant,

**Table 2**  
Formulation, preparation, and physicochemical properties of  $W_1/O/W_2$  emulsions stabilized by surfactants.

$W_1/O$			$O/W_2$		Size of $W_1/O/W_2$ droplet ( $\mu\text{m}$ )	Stable	References	
$W_1$	O	Surfactant	$W_2$	Surfactant				
Distilled water	Sunflower oil	PGPR (2.0 wt%)	Distilled water	Tween 20 (3.75 wt%)	10 -80 <sup>1*</sup> 25 <sup>1*</sup>	Yes (1 w, 4 °C)	Spyropoulos et al. (2019)	
				Sodium stearyl lactylate (SSL) (3.75 wt %)	5 -80 <sup>1*</sup> 19 <sup>1*</sup>	Yes (1 m, 4 °C)		
Skimmed milk (10.0 wt%), glucose (5.0 wt%), carrageenan (0.03 wt %)	Milk fat	PGPR (5.0 wt%)	Carrageenan (0.03 w/w %)	Skimmed milk (10.0 wt %)	31 <sup>*1</sup>	Stable (initially)	Klojdova et al. (2018)	
Skimmed milk (10.0 wt%), glucose (5.0 wt%), carrageenan (0.03 wt %)	Canola oil	PGPR (2.5 wt %) + sunflower lecithin (2.5 wt%)			34 <sup>*1</sup>	No		
Glucose (0.2 M)	Saturated medium chain triglyceride oil (MCT-oil)	Non-deoiled soybean lecithin (2.5 wt %) Non-deoiled sunflower lecithin (2.5 wt %) Phosphatidylcholine-depleted soybean lecithin (PC-depleted lecithin) (2.5 wt %)	Aqueous solution of glucose (0.2 M)	Whey protein isolate (WPI) (2.0 wt%)	30 <sup>*1</sup>	Yes (1 m, 5 °C)	Balcaen et al. (2021)	
					34 <sup>*1</sup>	Yes (1 m, 5 °C)		
					32 <sup>*1</sup>	Yes (1 m, 5 °C)		
	Long chain triglyceride-oil (LCT-oil) High oleic sunflower oil (HOSFO)	PC-depleted lecithin (2.5 wt %)			WPI (2.0 wt%) Carboxymethyl cellulose (CMC) (2.0 wt%) Powered soybean lecithin (2.0 wt%) Sodium caseinate (NaCas) (2.0 wt %)	58 <sup>*1</sup> 41 <sup>*1</sup>	Yes (1 m, 5 °C) Yes (1 m, 5 °C)	
						48 <sup>*1</sup>	Yes (1 m, 5 °C)	
					No DE <sup>2</sup>	-		
Grape seed phenolic-rich extract (10.0 wt%) Phosphate buffer (15 mM, pH 5.6)	Sunflower oil (SFO)	PGPR (4.0 wt%)	Phosphate buffer (15 mM, pH 5.6)	NaCas (1.0 wt%) NaCas (0.5 wt%) CMC (0.375% wt%) (NaCas-CMC) NaCas (0.5 wt%) Gum Arabic (0.5 wt%) (NaCas-GA)	6 -12* 9	Yes (14 d, room temperature)	Estevez et al. (2019)	
					6-12* 9	Yes (14 d, room temperature)		
					6-12* 9	Yes (14 d, room temperature)		
					6-12* 9	Yes (14 d, room temperature)		
Gallic acid (2–225 mg GA/kg DE)	Blend of olive, linseed and fish oil (70:20:10 w/w)	PGPR (6.0 wt%)	Quercetin nanoemulsion (2–225 mg Q/kg DE)	NaCas (0.5 wt%)	0.2-10 <sup>1</sup> (2.47) <sup>1</sup>	Yes (28 d, 4 °C)	Silva et al. (2018)	
					2–16 2.61 <sup>1</sup>	Yes (28 d, 4 °C)		
Water NaCl (0.4 wt%) Gelatin (10.0 wt%) NaCl (0.4 wt%) WPI (10.0 wt%)	SFO	PGPR (4.0 wt%)	NaCl (0.2 wt%)	WPI (1.0 wt%)	72.6 ± 2.7 <sup>3</sup> $\mu\text{m}$	Yes (7 d, 20 °C)	Oppermann et al. (2015)	
					67.7 <sup>3</sup> $\mu\text{m}$	Yes (7 d, 20 °C)		
NaCl (0.1 M Hydroxytyrosol (HTy) (375 mg/100 mL)	Perilla oil	PGPR (6.0 wt%)	NaCl (0.1 M)	NaCas (0.5 g/100 mL)	0.8–9.0* $\mu\text{m}$ 2.22 ± 0.10 <sup>1</sup> $\mu\text{m}$ Not reported <sup>4</sup>	Yes (22 d, 4 °C)	Flaiz et al. (2016)	
			NaCl (0.1 M), Gelatin (4.0 wt%) Transglutaminase (2.0 wt%)		Not reported <sup>4</sup>	Not reported <sup>4</sup>		
Solution of NaCl (0.1 wt%)	Isopropyl myristate (IPM) (4.9 w/w)	Blend <sup>6</sup> of Span 85-Tween 80 (2.1 w/w)			7.142 <sup>1</sup> $\mu\text{m}$	Yes (30 d, room temperature)	Wang et al. (2018)	
	MCT (4.9 w/w)				Blend <sup>6</sup> of Span 85-Tween 80 (2.1 w/w)	9.107 <sup>1</sup> $\mu\text{m}$		Yes (30 d, room temperature)
Blend of xanthan gum (XG) and locust bean gum (LBG) in a ratio of 4:6 w/w (0.5 wt%) Tea polyphenols (0.02 wt%)	Coconut oil (CO)	PGPR (2.0 wt%)	Xanthan gum (0.2 wt%)	Soybean lecithin (1 wt %)	12.1 <sup>1</sup> $\mu\text{m}$	Yes (28 d, 25 °C)	Tian et al. (2021)	

(continued on next page)

Table 2 (continued)

W <sub>1</sub>	W <sub>1</sub> /O		W <sub>2</sub>	O/W <sub>2</sub>	Surfactant	Size of W <sub>1</sub> /O/W <sub>2</sub> droplet (µm)	Stable	References
	O			Surfactant				
XG (0.5 wt%) Tea polyphenols (0.02 wt%) Deionized water (20 g) Tea polyphenols (0.02 wt%) Lactobacillus delbrueckii	Canola oil		Deionized water		Span-80 (10 v/v%)	12.2 <sup>1</sup> µm 12.8 <sup>1</sup> µm 0.5 to 1.30 <sup>1</sup> 0.35 to 31.7	Yes (28 d, 25 °C) Yes (28 d, 25 °C) Yes (7 d, room temperature) Yes (7 d, room temperature)	Eslami et al. (2017)
Acetate buffer solution (50 mM, pH 5.0) Ferrrous sulfate (2.5 wt%)	Rice bran oil (RBO) and rice bran stearin (RBS) (70:30 w/w)		Acetate buffer solution (50 mM, pH 5.0) 80.0 wt%		Quillaja saponin (2 wt %) Saponin (SA) (2 wt %)-chitosan (CHI) (0.3 wt%)	401.25 <sup>5</sup> ± 5.30 nm, +32.0 ± 0.3 mV	Tween 80 (2 v/v %) Yes (28 d, 25 °C)	0.35 to 31.7
Butyric acid (5.0 wt%) Milli-Q water	Soybean oil (SO)		No coating CHI (1.0 wt%) -Carboxymethyl cellulose (CMC) (1.0 wt%) coating (Chitosan (CHI) CHI (1 wt%)-CMC(1 wt%)-CHI-CMC coating		Tetra glycerin condensation ricinoleate (TGCR) (5.0 wt%)	16.9 <sup>5</sup> ± 0.7 µm 12.6 <sup>5</sup> ± 1.7 µm 15.4 <sup>5</sup> ± 1.5 µm	Yes (4 w, 25 °C) Yes (4 w, 25 °C) Yes (4 w, 25 °C)	Yamanaka et al. (2017b)

Note: (\*) Range of means derived from graphs. (1) corresponds to the D<sub>4,3</sub>. (2) For this system the enclosed water volume fraction was low, so it is not considered a DE. (3) The average sizes are reported as D<sub>0,5</sub>. (4) The gel does not allow droplet size determination (it cannot be diluted). (5) Droplet size is reported as D<sub>3,2</sub>. (6) The emulsifier blend was added to the oil phase. In the column of Stable\*, m = month(s), w = week(s), d = day(s), h = hour(s).

respectively. This set up allowed studying the surfactant interactions and visualizing the coalescence time between the W<sub>1</sub> and W<sub>2</sub> aqueous phases. Leister and Karbstein (2021) found that the time of coalescence of the droplet stabilized by Dehymuls PGPH (low HLB surfactant) was ≈15 s when 0.1 wt% of Lutensol TO8 (high HLB surfactant) was used. Meanwhile, 0.001 wt% of Lutensol TO8 increased the coalescence time to ≈60 s and to ≈40 s when Eumulgin B2 was used. It has been demonstrated that use of Tween 80 alone provided higher physical stability than β-cyclodextrins (Eslami et al., 2017). When Tween 80 was used, the droplet size did not change during storage, which suggests that Tween 80 provide higher stability against coalescence. However, β-cyclodextrins provided higher viability to microorganism than classic stabilization with Tween 80 surfactant. This can be an advantage for using DEs in nutraceutical products (Eslami et al., 2017) (Table 2).

In another study, Balcaen, et al. (2021) found that the stability of DEs changed depending on the type of high HLB surfactant used. The authors used different types of lecithin surfactants (e.g. native sunflower or soybean lecithin, phosphatidylcholine (PC)-depleted lecithin) in combination with a wide variety of high HLB surfactants (Table 2). Lecithin-based surfactants could stabilize both interfaces, but showed an improvement when a high HLB surfactant was used. The authors of the study assumed that the interfacial coverage of the HLB surfactant is responsible for this improved stability, being higher for carboxymethyl cellulose (CMC) and followed by whey protein isolate (WPI) and soybean lecithin. On the contrary, sodium caseinate (NaCas) only formed an O/W emulsion. The authors suggest that NaCas competitively displaced the lecithin from the oil-water interface, thus, external coalescence happened through holes on the droplets that were formed with a positive curvature.

The type of high HLB surfactant used also determines the size of the oil droplets and the yield of the dispersed aqueous phase (W<sub>1</sub>). Oppermann et al. (2018) used a small molecular weight surfactant, Tween 20, and two different proteins, Na-Cas and WPI. The authors suggest that the difference in the droplet size is related to the rate of interfacial adsorption and ability to decrease the interfacial tension, which also depends on the molecular structure of the surfactants. Therefore, Tween 20 presented smaller droplet size (51 µm), but higher yield values (100%). Differences were also found in terms of the proteins used. As WPI is a globular protein the rate of adsorption was lower, thus presented the lowest yield (65%) and higher droplet diameters (72 µm).

*Complex stabilization of the secondary emulsion (O/W<sub>2</sub>).* Besides the use of surfactants, complexes formed at the oil-water interface with various interfacial materials to improve the physical and diffusion stability of W/O/W DEs stabilized with surfactants have also been studied. Such complexes involve electrostatic interaction or covalent bonds between proteins and/or other biopolymers (Zembyla, Lazidis, et al., 2020, 2019a; Zembyla, Murray, et al., 2019; Zembyla, Murray, & Sarkar, 2020). These interactions are affected by the pH, ionic strength and biopolymer charge distribution (Dickinson, 2008). These multiple-layered protein-polysaccharide coatings around the oil generate electrostatic forces that enable the stabilization of oil droplets against aggregation, creaming and coalescence, because of steric effects and electrostatic repulsion (Estevez et al., 2019; Prichapan et al., 2021).

Fig. 4i and j shows the representation of complexes at the oil-water interface of DEs. Complexation not only improve the barrier properties of the oil-water interface, but also slowed down the diffusion of active compounds. For example, the structure and the oil droplet diameter in a W/O/W DEs did not change significantly with or without NaCas double coating, when carboxymethyl cellulose (NaCas-CMC) or gum Arabic (NaCas-GA) were used, during 14 days of storage at room temperature. Additionally, the retaining of hydrophilic active compounds was higher (Estevez et al., 2019) (Table 2). There was no difference between any of the polysaccharides used as both released around 19.6% ± 2.9 of the encapsulated polyphenol. On the contrary, single coating NaCas released 26% ± 3.6 of the entrapped polyphenol (Estevez et al., 2019).

In a recent study (Prichapan et al., 2021), saponin (SA) coated with

**Table 3**Formulation, preparation, and physicochemical properties of W<sub>1</sub>/O/W<sub>2</sub> emulsions stabilized by surfactants and particles.

W <sub>1</sub> /O			O/W <sub>2</sub>				Stable	Reference	
W <sub>1</sub>	O	Particle	Surfactant	W <sub>2</sub>	Particle	Surfactant			
Distilled water	SFO		PGPR (2.2 wt%)	Distilled water	Hydroxyl propyl methyl cellulose (HPMC) (3.75 wt%)	Tween 20 (3.75 wt%)	8-110* μm (28) <sup>2</sup>	No (1 m, 4 °C)	Spyropoulos et al. (2019)
					Rutin hydrate (RH) (3.75 wt%)		20-110* (60) <sup>2</sup>	Yes (1 m, 4 °C)	
					Colloidal carboxy methyl cellulose (CMCC) (3.75 wt%)		40-200* (100) <sup>2</sup>	No (1 m, 4 °C)	
					Ethylcellulose (2.2%) (EC)		-	No stable DE	
Deionized water	Squalane		Soybean lecithin (1 w/v%)	Deionized water	Zein particles (1 w/v%) <sup>3</sup>	-	≈20*	Yes (7 d, room temperature)	Jiang et al. (2021)
Zein particles (1.0 w/v %)									
Gelatin (1.5 wt%)	SO		PGPR (2.0 wt%)	Water	Kafrin particles (1.5 wt%)		5-85 (48) <sup>2</sup>	No (14 d, room temperature)	Xiao et al. (2017)
Anthocyanin (0.05 wt %)									
Citric acid buffer (0.01 M, pH 3.4)									
Anthocyanin (2.0 w/v%) in deionized water	SO		PGPR (2.0 w/v%)	Water deionized	Octenylsuccinate anhydride modified quinoa starch (OSQS) (6 w/v%)		10-100 <sup>±1</sup> (32) <sup>2</sup>	Yes (7 d)	Lin et al. (2020)
Saccharose (2 w/v%)	Corn oil		PGPR (5.0 w/v%)	Distilled water (pH 5.5)	Gliadin nanoparticles (1.5 w/v %)		NR	Yes (30 d, 4 °C)	Xing et al. (2018)
Gelatin (5 w/v %, pH 5.5)	Quercetin (1 mg/g)								
Catechin (-)-epigallocatechin-3-gallate (EGCG) (0.4 wt%)									
Phosphate buffer (5 mM, pH 7.0)	Liquid shea nut oil		PGPR (5.0 w/v%)	Phosphate buffer (5 mM, pH 7.0)	Heat treated OSQS		27.4 <sup>1</sup>	Yes (Freeze-thaw cycling)	Marefati et al. (2015)
NaCl (0.2 M)					Non heat treated OSQS		11.3 <sup>1</sup>	Yes (Freeze-thaw cycling)	
Carmine (marker)	Solid shea nut oil				Heat treated OSQS (214 mg/mL)		42.7 <sup>1</sup>	Yes (Freeze-thaw cycling)	
					Non heat treated OSQS (214 mg/mL)		11.8 <sup>1</sup>	Yes (Freeze-thaw cycling)	
NaCl (141 mM)	SFO		PGPR (2.8 wt%)	Deionized water	Waxy maize starch (4 wt%)			No (90 d)	Chiu et al. (2017)
					OSA-waxy maize starch (4 wt%)		18-25 <sup>1,4</sup>	Yes (90 d)	

Note: (\*) Data derived from the graphs. <sup>(1)</sup> Data correspond to the D<sub>3,2</sub> values. <sup>(2)</sup> This value represents the mean value of the distributions. DE = double emulsion. <sup>(3)</sup> Zein particles form a complex with lecithin to stabilize the high internal phase Pickering emulsion <sup>(4)</sup> Highest for the emulsion stabilized with untreated starch and lowest for the emulsion stabilized with 3 wt% OSA starch. NR= Not reported. In the column of stable, m = month(s), w = week(s), d = day(s), h = hour(s).

chitosan (CHI) exhibited very low mean diameter of the oil droplets of a W/O/W DE with size ranging from 390 to 400 nm when the concentration of CHI was between 0.3 and 0.4 wt% and no phase separation was observed (Table 2). A lower concentration of CHI resulted in higher oil droplets size (≈19-15 μm) and phase separation. Regarding diffusion stability, SA-CHI coatings (87.0 ± 0.7% encapsulation efficiency) retained more efficiently the encapsulated ferrous sulfate than the single layer saponin (76.7 ± 0.2% encapsulation efficiency). In addition, the diffusion of water was hindered by the presence of a double coating. However, once this phenomenon led to the swelling of the water droplets, the release of the ferrous sulfate was significantly increased, mainly by the breakdown of the W/O emulsion (Table 2). Double coating also enabled higher stability under osmotic stress compared to single coatings (Prichapan et al., 2021).

Several layers of coating can be created, with a small increase in the droplet size with each layer, from 12.1 μm (single coating) to 15.3 μm (CHI-CMC-CHI-CMC) (Table 2). This was proposed by Yamanaka et al. (2017a), who made multiple coating layers with modified-lecithin and CHI or CMC in sequence (CHI-CMC-CHI-CMC). The storage stability of this structure was found to be similar to the ones reported with SA, as the droplets size barely changed over time. It is worth noticing that double saponin coatings were subjected to an osmotic stress; thus, the same measurements should have been performed on CHI-CMC-CHI-CMC for a fair comparison (Table 2). One of the valuable applications for CHI-CMC and CHI-CMC-CHI-CMC is that this type of coating can be designed to resist harsh conditions, such as the pH in the stomach and target release in the intestines for bioactive molecules.

**Table 4**  
Formulation, preparation, and physicochemical properties of  $W_1/O/W_2$  emulsions stabilized solely by particles.

$W_1/O$			$O/W_2$		Emulsification method	Size of $W_1/O/W_2$ droplet ( $\mu\text{m}$ )	Stable	Reference
$W_1$	O	Particle	$W_2$	Particle				
Distilled water	Sunflower oil	Ethylcellulose (EC) (2.2 wt%)	Distilled water	Hydroxypropyl methyl cellulose (HPMC) (3.75%)	Two-steps	3-130* (40) <sup>2</sup>	Not stable	Spyropoulos et al. (2019)
				Rutin hydrate (RH) (3.75%)		10-100* (59) <sup>2</sup>		
				Colloidal microcrystalline cellulose (CMCC) (3.75%)		-	Not stable	
Particle suspension (pH 6)	Algal oil	Corn-peptide-functionalized calcium phosphate (CP-CaP) (1.28 wt%)			One-step	5-70 <sup>3*</sup>	Yes (1 m at room temperature)	Ruan et al. (2018)

Note: (\*) The data derive from the graphs and (<sup>1</sup>) is the mean diameter of oil droplets that decrease upon increasing the homogenization speed from 10,000 to 18,000 in  $W/O/W$  multiple emulsions containing 1 wt% of both particle types with  $\Phi_{w/o} = 0.1$  and  $\Phi_g = 0.47$ . (2) The data corresponds to the mean  $D_{3,2}$  values. DE = double emulsion. (3) The droplet size depends on the pH of the system: for pH 4.0,  $D_{4,3} = 30.6 \mu\text{m}$ , pH 5.0,  $D_{4,3} = 22.1 \mu\text{m}$ , pH 6.0,  $D_{4,3} = 23.6 \mu\text{m}$ , pH 7.0,  $D_{4,3} = 12 \mu\text{m}$ . In the column of stable, m = month(s), w = week(s), d = day(s), h = hour(s).

### 3.2. Polyglycerol polyricinoleate replacement

Unfortunately, there are not many food grade surfactants to stabilize the primary emulsion (W/O), thus, PGPR has become the most widely use surfactant (Table 2). PGPR provides sufficient stability to the primary emulsion (W/O) and has been accepted as food-grade surfactant (Dickinson, 2011). Nevertheless, consumers are looking for natural and clean-label options. Therefore, few attempts have been done to eliminate partially or completely PGPR from formulations and replace it with other surfactants that can stabilize the water-oil interface, such as different types of lecithin and phosphatidylcholine depleted lecithin (PC-depleted lecithin) (Balcaen et al., 2021). These surfactants could stabilize DEs although the stability of these emulsions depended strongly on the type of oil used, with MCT showing the best results. However, no DEs was formed when 2.5 wt% of PGPR was combined with 2.5 wt% of sunflower lecithin, even in the presence of carrageenan (Klojdova et al., 2018) (Table 2).

Nonetheless, many parameters interfere with the final structure and stability of DEs, as demonstrated in another experiment done by Leong et al. (2018),  $W/O/W$  emulsions were formed when 1.0 wt % of PGPR was used with 2.0 wt% of soy lecithin as low HLB surfactant. The major challenge found was the significant release of NaCl, which was added to the  $W_1$  as a marker of the diffusion of water, during storage: thus, the authors established that in order to have greater diffusion stability, 5 wt % of PGPR was required. There has been some recent efforts to replace PGPR using natural organic crystals (e.g. curcumin, quercetin), combination of such crystals and biopolymers and/or microgels for  $W/O$  emulsions (Zembyla, Lazidis, et al., 2019, 2020a; Zembyla, Murray, et al., 2019; Zembyla et al., 2018, 2020b) but such strategies have not been extended to DEs to date.

### 3.3. Bulk stabilization

Gelling the aqueous phases (either the inner ( $W_1$ ) or the outer ( $W_2$ ) aqueous phase) or the dispersed oil phase have also been commonly used as strategies to control the diffusion phenomena of the primary emulsion ( $W_1/O$ ) in  $W/O/W$  DEs (Fig. 4k and l). The advantage of this strategy is that it helps to maintain the multifaceted functions of DEs (encapsulation, and improvement of sensorial characteristics in low-fat products).

*Gelling of the  $W_1$ .* Gelling the inner phase  $W_1$  (Fig. 4k) has shown to enhance the diffusion stability of  $W/O/W$  DEs which has a significant improvement on the overall microstructural stability. A series of studies (Table 2) have shown that gelling the inner aqueous droplets enhanced

the yield of water entrapped in the oil, the retention of water, the resistance to coalescence of the internal droplets and the resistance to external shear, temperature and osmotic conditions (Klojdova et al., 2018; Oppermann et al., 2015; Tian et al., 2021). Having a higher yield is relevant for designing low fat-products as this allows replacing a higher amount of oil. Oppermann et al. (2016) proposed to reduce fat content by using different  $W_1$  fractions of the primary emulsions ranging from 30 to 50 wt%. After processing, they managed to replace 27.8–46.9 wt% of fat, when gelatin was used as a gelling agent of the inner droplets (see the microstructure in Fig. 5b).

Oppermann et al. (2015) found that the type of gel used presented differences in the yield value and water retention over time (Table 2). The gelation of the inner water droplets has shown a higher yield value with WPI (100%) compared to gelatin (90%), but both presented good resilience against destabilization when subjected to high shear and heat treatment conditions when compared with the un-gelled counterparts. Nevertheless, fine-stranded networks such as gelatin allow absorbing water from the external aqueous phase ( $W_2$ ) during storage; thus, the water yield increases, eventually generating the breakage of the oil droplets. However, the yield remained stable with WPI, which have a coarse-stranded network. In a subsequent study, Oppermann, et al. (2018) found that inner droplets gelled with gelatin did not have a significant effect on the size of the oil droplets, as this is determined by several parameter, such as the type of high HLB surfactant, viscosity ratio and thickener used in the  $W_2$  phase. Besides proteins, polysaccharides have also been used as gelling agents of the inner water phase. For example, Tian, et al. (2021) gelled the  $W_1$  with XG and a blend of XG and locust bean gum (LBG). The authors found that the blend of XG + LBG presented stronger stability during storage, higher retention and protection of bioactive compounds (Table 2). The increase of the viscosity of the  $W_1$  phase by the blend of XG + LBG reduced the breakup of the droplets during the emulsification process; thus, the oil droplet size was slightly higher.

*Gelling of the  $W_2$ .* When the external aqueous phase ( $W_2$ ) (Fig. 4l) is gelled, emulsions have also shown higher stability against flocculation, coalesce and diffusion. In fact, hydrogel networks immobilize both the oil droplets and the aqueous molecules within the  $W_1$  aqueous phase (Farjami & Madadlou, 2019). However, this has been shown to be concentration dependent, in other words, it depends on the overall gel content in the DEs. For instance, a 0.03 wt% of carrageenan in the continuous aqueous phase ( $W_2$ ) has been shown to provide physical stability to  $W/O/W$  DE, whereas a lower (0.02 wt%) or a higher (0.04 and 0.05 w%) concentrations were not enough to improve its storage stability, as the droplets size of DEs significantly increased due to

**Table 5**Formulation, preparation, and physicochemical properties of W<sub>1</sub>/O/W<sub>2</sub> emulsions stabilized by surfactants and fat networks.

W <sub>1</sub> /O		O/W <sub>2</sub>		Type of fat stabilization	Size of W <sub>1</sub> /O/W <sub>2</sub> droplet (μm)	Stable	Reference		
W <sub>1</sub>	O	Solid lipid-based gelator	Surfactant					W <sub>2</sub>	Surfactant
Ultrapure water/ Tartrazine (40 mg/L)	Corn oil	Glycerol monostearate (GMS) (10 wt%)	PGPR (10.0 wt %)	Ultrapure water Sodium Ca-alginate hydrogel (1.0 wt%)	Tween 80 (3.0 wt%)	Crystal shells (Pickering stabilization)/crosslink stability	1.17 <sup>2</sup>	Yes (24 h, 50 °C)	Sun et al. (2019)
				Ultrapure water		Crystal shells (Pickering stabilization)	5.7 <sup>1</sup>	No (24 h, 50 °C)	
Anthocyanin solution Phosphate buffer (5 mM, pH 3.0)	SO (95.0 wt%)	-	PGPR (5.0 wt%)	Phosphate buffer solution (5 mM, pH 3.0)/Gum Arabic (2.5%)	Quillaja saponin (1.0 wt%)	Surfactant stabilization	33.5	-	Liu, Zhou, et al. (2020)
	-	Hydrogenated soybean oil (95 wt%) (HSO)				Pickering stabilization	46.2 <sup>1</sup>	Yes (14 d, room temperature)	
NaCl (0.1M)	Olive oil (97.0 wt %)		PGPR (3.0 wt%)	Aqueous solution of NaCl (0.1M)	NaCas (0.5 wt%)	Lyotropic liquid crystals	1.96 <sup>1</sup>	Yes (8 d at 4 °C)	Fernandez-Martin et al. (2017)
	Olive oil (94.0 wt %)	Blend of mono- and di-acylglycerides (3.0 wt%) (V10)					2.19 <sup>1</sup>	Yes (8 d at 4 °C)	
	Olive oil (94.0 wt %)	Blend of mono- and di-acylglycerides (3 wt%) (V50)					1.94 <sup>1</sup>	Yes (8 d at 4 °C)	
MgCl <sub>2</sub> (0.1M)	-	Anhydrous Milkfat (AMF) (98%)	PGPR (2.0 wt%)	Glucose (3.0 wt%)/XG (0.5 wt%)	NaCas (3.0 wt%)	Core-solid shell at the interface of the double emulsion droplets	18 <sup>1</sup>	Yes (1 m at 4 °C)	Herzi and Essafi (2019)
MgCl <sub>2</sub> (0.1M)	MCT oil (0–100 wt%) -	Cocoa butter (CB) (0–100 wt%)	PGPR (5.0 wt%)	Lactose (0.3 M)/XG (0.5 wt %)	NaCas (3.0 wt%)	Fat network	10.2 <sup>1</sup>	Yes (1 m at 4 °C)	Herzi and Essafi (2018)
		AMF (98 wt%)	PGPR (2.0 wt%)	Glucose (0.3 M)/XG (0.5 wt %)		Crystalline shell	18 <sup>1</sup>	Yes (1 m at 4 °C)	
KCl (0.1 M)		Soft palm mid fraction (95 wt%) (sPMF)	PGPR (5.0 wt%)	Aqueous solution of KCl (0.1 M) XG (0.3 wt%)	NaCas (1.25 wt%)	Fat network	25	Yes (1 m at 5 °C)	Nelis, Declerck, et al. (2019)
		HOSFO (95.0 wt %)				-	29	Yes (1 m at 4 °C)	
NaCl (0.5 M)		AMF		D-glucose (0.8 M)	NaCas (12.0 wt%)	Pickering and network stabilization	22.5	Yes (21 d at 4 °C)	Goibier et al. (2020)
KCl (0.1 M)		sPMF (95.0 wt%)	PGPR (5.0 wt%)	KCl (0.1M wt %)	NaCas (1.25 wt%)	-	2.5 <sup>1</sup>	-	Nelis, Declerck, et al. (2019)
		Partially hydrogenated sunflower oil (PHSO) (95 wt%)		XG (0.3 wt%)		-	25 <sup>1</sup>	-	
NaCl (0.5 M) Sodium alginate (2.0 wt%) Chlorophyllin (112 ppm)	MCT	Glyceryl stearate (GS)	PGPR	NaCl (0.5 M)	Tween80 (2.0 wt%)		11.09 ± 5.71	Yes (12 d at 4 °C)	(Molet-Rodríguez et al., 2021)
	Corn oil	GS		Sodium alginate (2.0 wt%)			9.06 ± 1.96	Yes (12 d at 4 °C)	
	MCT	GS			Lecithin (2.0 wt%)		7.35 ± 0.68	Yes (12 d, 4 °C)	
	Corn Oil	GS					7.64 ± 0.45	Yes (12 d, 4 °C)	
	MCT	-			Tween80 (2.0 wt%)		9.90 ± 0.15	Yes (12 d, 4 °C)	
	Corn oil	-					13.14 ± 1.51	Yes (12 d, 4 °C)	
	MCT	-			Lecithin (2.0 wt%)		- <sup>3</sup>	No (12 d, 4 °C)	
	Corn oil	-					14.54 ± 0.14	Yes (12 d, 4 °C)	

Note: (\*) Range of means derived from graphs distributions for emulsions. <sup>(1)</sup> Corresponds to the D<sub>4,3</sub>. <sup>(2)</sup> This value correspond to double emulsions without sodium ca-alginate hydrogel. <sup>(3)</sup> Not DEs. In the column of stable, m = month(s), w = week(s), d = day(s), h = hour(s).

aggregation phenomena (Klojdova et al., 2018) (Table 2, see the micrograph in Fig. 5c).

Another study where gelation of the outer  $W_2$  phase has been shown to improve the physical stability of DEs was performed by Flaiz et al. (2016). In this study, an acceptable physical stability was reported when gelatin was combined with the enzyme transglutaminase to form a thermostable gel (Table 2), as no phase separation was observed. Due to the covalent bonds formed in the hydrogels with gelatin and transglutaminase, the DEs with gelled  $W_2$  showed better encapsulation efficiency of the hydrophilic polyphenol hydroxytyrosol (HTy) when compared with the un-gelled counterparts and simple emulsions. During storage, gelled DEs presented improved stability with respect to release of the HTy than un-gelled DEs. The levels of HTy decreased to 24.2% and 26.9% of the initial concentration, in the gelled and un-gelled DEs, respectively. However, when the HTy was added in the water continuous phase of a simple emulsion, the concentration of HTy decreased to 8.6%, which might be linked to the higher compartmentalized system in DEs. Although there are separate studies on complex formation involving biopolymers and gelling of water phases, there are no study that has compared the stability of DEs when the same biopolymer (e.g. WPI) is present as a complex with the surfactant versus when it is only a gelling agent in either of the  $W_1$  or  $W_2$  phases. Such comparative data in the future can help using the right design strategy for more stable DEs with optimum release kinetics.

### 3.4. Particle stabilization

Double Pickering emulsions (DPEs) where DEs are stabilized by particles have been gaining attention in the food industry in the last few years, because of their high thermodynamic stability. In DEs Pickering particles can stabilize the primary emulsion (Fig. 4c), the external phase (Fig. 4d) or both of them using a single or different types of particles for each phase (Fig. 4e and f). Particles are normally combined with surfactants and most of the research focuses on the stabilization of the secondary emulsion ( $(W_1/O)/W_2$ ) using particles (Table 3). In contrast, there are a few reports of DPEs that are solely stabilized by particles (Table 4). Some particles that have been used in the literature as stabilizer for the secondary emulsion include zein particles, kafirin particles, octenyl succinic anhydride (OSA) starch (obtained mainly from quinoa, but also from waxy maize starch), rutin hydrate (RH) particles, hydroxypropyl methyl cellulose (HPMC) particles, colloidal microcrystalline cellulose (CMCC) and gliadin nanoparticles (GNP) (Table 3). Meanwhile, only three different types of particles have been reported as stabilizers of the primary emulsion: yellow pigment (PY), corn-peptide-functionalized calcium phosphate (CP-CaP) and ethylcellulose (EC) and the corresponding microstructures of these DPEs can be observed in Fig. 5d–f.

*Pickering particles for the  $O/W_2$  emulsion stabilization.* Unlike conventional Pickering particles, organic particles do not provide the same degree of stability as offered by most inorganic particles such as silica, calcium carbonate, hydroxyapatite (Hap), among others. This lower stability is associated with the rather poor wettability of the nature-derived particles (Chen et al., 2020). For example, zein particles cannot stabilize the interface of  $O/W$  Pickering emulsion with high internal phase for more than five days (phase separation occurred). Furthermore, zein particles cannot hold the DEs structure during a two-step production process; thus, a phase inversion to  $O/W$  emulsion is obtained. It has been observed that the formation of complexes of particles with other surface-active materials provides higher stability to food-grade particles obtained from natural sources. For instance, lecithin (1 w/v%) and zein particles (1 w/v%) form a complex that provide highly stable interfaces and thus DPEs can be formed (Table 3). This complex can support a DE with oil volume fraction up to 0.85 (Jiang et al., 2021).

When using Pickering particles obtained from natural sources to stabilize DEs, diffusion still remains a key concern due to difference in

the osmotic pressure between the dispersed and continuous aqueous phase. Xiao et al. (2017) and Lin et al. (2020) reported a significant decrease in the active compound encapsulated (anthocyanin) in the  $W_1$  aqueous phase, because of this difference in the osmotic pressure (Table 3). For DPEs stabilized by PGPR for the primary emulsion and octenylsuccinate quinoa starch (OSQS) for the external emulsion, the water droplets were swollen with the external water phase, while the anthocyanin was significantly released (up to a 60% loss) after 7 days of storage (Lin et al., 2020). The same behaviour was observed when using kafirin as Pickering particles. In fact, the DEs inverted to simple  $W/O$  emulsions after 14 days of storage at room temperature (Xiao et al., 2017). The difference in osmotic pressure between the aqueous phases remains a bottleneck in DPEs, despite of the high energy of attachment of Pickering particles. Nevertheless, as in surfactant-stabilized DEs, the diffusion instability can be controlled by the same strategies used in only surfactant systems, such as gelling of the aqueous phase, partial crystallization of the oil phases or balance of the osmotic pressure. For example, Xing, et al. (2018) designed gelled DPEs that showed higher physical and diffusion stability by adding 5 w/v% of gelatin in the inner aqueous phase (Table 3). They used gliadin nanoparticles (GNP) to stabilize the secondary emulsion in GDPEs, which in combination with gelatin as a gelling agent of  $W_1$ , enhanced the stability against release of encapsulated catechin (–)–epigallocatechin-3-Gallate (EGCG) and quercetin under simulated intestinal fluids conditions (8 h). This enhancement may be related to the dual stabilization strategy *i.e.* formation of a shell of GNP around the oil droplets (*i.e.* particle stabilization) and the gelled state of the inner droplets (*i.e.* bulk inner phase stabilization), which prevented coalescence and phase diffusion, respectively. DPEs stabilized with a complex of zein particles and lecithin has also shown a high protection against gastrointestinal fluids (around 120 min of digestion) (Jiang et al., 2021) (Table 3).

Fig. 5 shows the micrographs of three different particles used to stabilize the secondary  $O/W$  emulsion in DPEs: kafirin particles (Fig. 5g), OSA quinoa starch particles (OSQS) (Fig. 5h) and wheat gliadin nanoparticles (Fig. 5i). In all cases, PGPR has been used to stabilize the  $W/O$  emulsion in the first step. As it can be seen, the size of the droplets differ between them, being higher for OSQS and kafirin particles as compared to gliadin nanoparticles. This is expected as the size of the droplets is affected by the size of the particles stabilizing the droplets (Saari et al., 2016), as gliadin nanoparticles and kafirin (100–300 nm) were significantly lower in size compared to OSQS (0.5–3  $\mu\text{m}$ ) (Saari et al., 2016; Xiao et al., 2017; Xing et al., 2018). The distribution of the Pickering particles at the interface of the oil droplets might also dictate the stability of the DPEs. For example, it was observed by cryogenic-scanning electron microscopy (cryo-SEM) that the kafirin particles do not cover completely the oil-water interface, thus, they provide lower stability (Xiao et al., 2017).

Chemical modification of food-grade particles have been used to improve the efficiency of food grade particles as Pickering stabilizers. For instance, the hydrophilic behaviour of starch can be altered using a pre-treatment with OSA. The incorporation of octenyl molecules results in starch granules with amphiphilic properties due to the esterification. When starch was esterified to about 2.5–3 wt% with the OSA, the droplet size of OSQS stabilized DEs did not change during up to 90 days of storage, while DPEs containing 0.5 wt% of OSQS esterification presented higher levels of coalescence of the external oil droplets at 3 days of storage (Table 3).

The diameter of DPEs can be also manipulated by the degree of esterification, with lower size of droplets reported with higher degree of OSA substitution. Oil droplet diameters decreased from 25  $\mu\text{m}$  for DPE without OSA substitution to 19  $\mu\text{m}$  for 3 wt% of substitution (Chiu et al., 2017). Work done by Lin et al. (2020) found that DEs stabilized with OSA-quinoa starch particles (OSQS) released 60% of the encapsulated anthocyanin after 7 days of storage. However, Marefati, et al. (2015) designed DPEs with OSQS (degree of esterification of 1.8) by partially gelling the OSQS particles at the interface (see schematic illustration in

Fig. 4b). The partial gelation was achieved when the DEs was subjected to a thermal process (1 min at 70 °C). This process boosted encapsulation stability, as these DPEs formulations resisted to freezing and freeze-drying process. When a solid oil phase (solid shea nut oil) was used, a higher resistance to stresses was observed, with and without thermal modification of the OSQS. However, for a liquid oil (liquid shea nut oil), the thermal process on OSQS DPEs provided higher stability to processing conditions, and acted as a protective barrier at the surface of the oil droplets (Fig. 4b). The encapsulation stability of different variations of heat-treated OSQS was remarkable, having values of retention of over 97.3% of the entrapped encapsulated compound (Carmines) (Marefati et al., 2015).

It is important to note that the stability of the DEs can be controlled depending on the desired application. OSA starch based DPEs can have enough stability, but at the same time they allowed the release of internally encapsulated compounds (e.g. sodium) orally through action of  $\alpha$ -amylase and starch degradation (Torres et al., 2018), therefore allowing high levels of salt perception (Chiu et al., 2017). When the requirement is to reduce the salt content in a food product maintaining similar taste, 1.5 wt% of OSA treatment in starch is enough to fulfil the aim. However, if the aim of the DE is to protect active compounds against gastric condition, then the formulation and design must be done to resist such conditions.

For surfactant/Pickering particle DEs, being the surfactant the stabilizer for the primary emulsions and the Pickering particle the stabilizer for the secondary emulsion, the concentrations of surfactant plays an important role on the overall stability of the DPEs (Table 3). It was reported that higher concentrations of PGPR decreased the encapsulation efficiency (EE) (Xiao et al., 2017) and smaller droplets were formed (Lin et al., 2020; Xiao et al., 2017). The decreased EE was attributed to the excess of PGPR (higher than 2 wt%), which hinders the stability of the DPEs. This behaviour might be attributed to: 1) the competition between PGPR and particles for the same interface or 2) the adsorption of PGPR on the particle (Xiao et al., 2017). Nevertheless, the exact interaction mechanism between PGPR and the different particles is still not fully understood, as Lin et al. (2020) did not find significant differences for higher concentrations of PGPR in a PGPR/OSQS-stabilized DPEs.

*Pickering particles for  $W_1/O$  primary emulsion stabilization.* In opposition to  $O/W_2$  emulsion stabilization, Pickering particle/surfactant research is almost inexistent for DEs, and, to the best of our knowledge, there is only one article to date that reports the use of ethylcellulose (EC) as Pickering particle in the primary emulsion and surfactants to stabilize the secondary interface. With this advent of new materials to stabilize the water-oil interface (Zembyla, Lazidis, et al., 2019, 2020a; Zembyla, Murray, et al., 2019; Zembyla et al., 2018, 2020b), DPEs could gain more attention in the food industry. A recent work (Spyropoulos et al., 2019) evaluated the stability of EC particles and three different high HLB surfactants: Tween 20, sodium stearyl lactylate (SSL) and NaCas. Of these three particle/surfactant systems, only EC/SSL formed stable emulsions, while the other emulsions barely stayed stable for few hours before phase separation occurs. However, the exact stabilization mechanism or the interaction between particles and surfactants in these systems remains elusive and needs further investigation.

Recently, there has also been an increasing interest for the development of particles to stabilize water/oil interfaces. Some examples are polyphenol crystals (curcumin and quercetin), zein particles, starch mixed ester nanoparticle, lignin particle, cellulose nanocrystal/nanofiber and oleosomes (Sarkar & Dickinson, 2020). It was also observed that the use of other surface-active species, such as proteins modify the particle surface, and thus the complex formed improves the attachment to the interfaces. Nonetheless, to date, this type of particle complex has only been studied in simple  $W/O$  emulsion (Zembyla, Lazidis, et al., 2019, 2020a; Zembyla, Murray, et al., 2019; Zembyla, Murray, & Sarkar, 2020). Fat crystals with surface activity are also capable of stabilizing water-oil interfaces (see Table 5 and following Section 3.5 for further details); however, this is a relatively new trend and only anhydrous milk

fat (AMF) (Fig. 5k) has been reported to stabilize DEs by Pickering stabilization due to forming a shell, that demonstrated high stability against phase diffusion (Goibier et al., 2020). However, further research is needed to elucidate the stabilization mechanism and thus, confirm Pickering stabilization for this system.

*Pickering particles for  $W_1/O/W_2$  stabilization.* Unlike the examples cited in Table 3 where several particle and surfactant system are combined to produce DPEs; Table 4 shows only three different systems where DEs have been fabricated solely using particles (Fig. 4e and f). Within the  $W/O/W$  emulsions, only one study to stabilize the  $W_1/O$  (EC), three for the  $O/W_2$  interface (HPMC, RH and CMCC) and one option to stabilize both interfaces with particles are shown. The physicochemical properties of particles play an important role in the control of the stability of DPEs. For instance, EC/RH DPEs presented an acceptable stability (1 month at 4 °C), but EC/HPMC and EC/CMCC could form only highly unstable DEs that reverted to a simple  $O/W$  emulsion after processing (Table 4). Although this behaviour might be related to the competition for the same interface (Spyropoulos et al., 2019), multiple phenomena occur at the same time, including diffusion related to osmotic pressure. Thus, if a balance is not created between both aqueous phases, the overall stability of the DPEs might be hindered leading to water diffusion. Thus, further research needs to be performed in order to understand the relationship between different particles in the two interfaces of DEs.

Interestingly, DPEs stabilized with just one type of particle (Fig. 4e) have been engineered by modifying the surface properties of the particles with impurities contained in the oil, instead of by chemical treatments, as shown by the work of Ruan et al. (2018). Using a one-step method (Table 4), oil impurities were used to change the contact angle of the particle while the aqueous and oil phases were being mixed (as previously discussed in the one-step method in the phase inversion section). Thus, some of the hydrophobic CP-CaP particles used stabilized the  $W_1/O$  interface, while others were hydrophobized by the impurities. This mechanism allowed the formation and stabilization of the second emulsion (Fig. 1b). The pH of the aqueous phase also determines the droplet size and the structure of the emulsion, with gelled emulsions being generated at pH 5.0 or 6.0, and homogeneous emulsions created at pH 4.0 and 7.0. It was also found that the higher the pH of the aqueous solution, the lower was the size of the droplets (Table 4).

### 3.5. Fat crystals for bulk stabilization

One prominent strategy to improve the stability of DEs is to partially solidify the oil phase by adding a structuring agent to partially crystallize it (Fig. 4g and h). In DEs, crystallized oils have provided higher stability against diffusion which have also increased the encapsulation efficiency of active compounds (Herzi & Essafi, 2019; Liu, Zhou, et al., 2020; Molet-Rodríguez et al., 2021; Nelis, Declerck, et al., 2019). These structuring agents are known as fat gelators. Normally, fat gelators solidify in the oil phase forming crystals that create a compact and stable network. Table 5 shows some formulations that have used gelators to stabilize DEs. As can be seen, glycerol monostearate (GMS), hydrogenated soybean oil (HSO), glyceryl stearate (GS), cocoa butter (CB) and mono- and di-acylglycerides have been most commonly used as gelators for  $W/O/W$  DEs. Soy palm mid fraction and anhydrous milk fat (AMF) are examples of fat that do not need gelators but can form semi-solid crystalline structures on their own in DEs (Table 5).

In DEs, it was found that fat crystals could stabilize the system by two different types of mechanisms: forming a fat network in the bulk oil phase (Fig. 4g) or acting as Pickering stabilizers (Fig. 4h), though the exact mechanism is sometimes difficult to understand. Table 5 reports the conferred type of stabilization according to the gelator used. It is worth noting that the majority of the research reported a Pickering stabilization behaviour of the solid crystals used to stabilize the water-oil interface. Different conditions of processing and cooling can result in different polymorphic structures, with different melting points and



thus confer various degree of stability. Whether a fat crystal act as Pickering or network stabilizer depends on the ability of fat crystals to adsorb at the interface. While monoacylglycerols (MAGs) are amphiphilic crystals that can stabilize the water-oil interface, fully saturated fat crystals do not present surface activity, thus, they generally tend to confer network stability. (Ghosh & Rousseau, 2011).

**Fat crystals for Pickering stabilization.** In a Pickering stabilization, the crystals should locate at the interface of the oil droplet, thus forming a shell around it. This characteristic provide a higher diffusion stability. For instance, Herzi and Essafi (2018) evaluated the diffusion stability in DEs formed by using a blend of MCT with CB and AMF (Fig. 5k). Although both fats form crystals and provide higher stability against the diffusion of the  $Mg^{2+}$  ion encapsulated in the  $W_1$  aqueous phase (Table 5), the release of  $Mg^{2+}$  was higher in the blend of CB:MCT than with AMF indicating that crystallization of the oil phase by using AMF improved the stability of the DEs against diffusion. Herzi and Essafi (2018) conclude that different mechanisms of stabilization were present as the release of  $Mg^{2+}$  in CB systems depended on its concentration (the higher the concentration of CB, the lower the rate of release of the ion), while AMF blocked the release of  $Mg^{2+}$ , which remained constant at 13% of the  $Mg^{2+}$  release, independently of its concentration. Thus, both fat network (Fig. 4g) and Pickering stabilization (Fig. 4h) are expected to provide stability (and encapsulation efficiency) when using CB and AMF, respectively.

The effectiveness of fat crystals as Pickering particles depends on their size, shape, concentration, composition, hydrophobicity and wetting behaviour (Ghosh et al., 2011). One would expect that fat crystal would be able to stabilize the primary emulsion (W/O) and even resist the second step of manufacturing of DEs. In fact, recently this has been probed by Goibier et al. (2020), who designed DEs stabilized solely by fat crystals. Though they only report results for AMF, they were also able to form DEs by using other solid-fats such as palm oil, CB and coconut oil (CO). The droplet size of the primary emulsions reported were sufficiently small to produce acceptable size of oil droplets, which are in the range of some DEs stabilized using surfactants (Table 2). The stability to swelling was also remarkable during 7 days of storage at 4 °C. Thus, it is proposed that the AMF crystals form a shell around the water-oil interface (Goibier et al., 2020) (Table 5, Fig. 4h).

**Crystals for network stabilization.** Besides Pickering stabilization, fat networks may also stabilize the oil droplets by an arrangement of crystals that surrounds the dispersed aqueous phase (Fig. 4g). Stability by fat networks require a minimum of 5 wt% of solid fat (Ghosh & Rousseau, 2011). Besides the inherent triacylglycerol (TAG) composition, the type and properties of the possible crystal structures can affect the stabilization of DEs (Sato, 2001) (Table 5). For instance, during cooling of a DE stabilized with 5 wt% of PGPR, the high content of *trans*-fatty acids (C18:1 *trans*) of the hydrogenated sunflower oil (PHSFO) promoted the initial formation  $\alpha_1$  crystals and a relatively quick transformation to the  $\beta'$  polymorph. Meanwhile, the same polymorphic transformation was slower for soft palm mid fraction (SPMF), which has a high content of C16:0 fatty acids (Nelis, Declercle, et al., 2019). In both cases the liquid/solid and  $\alpha/\beta'$  transitions were slower in the DEs than in the corresponding bulk fat/PGPR mixture. Additionally, differences in the structure of the  $\alpha$  polymorphs form in the DEs compared to the bulk were observed. These have been attributed to the ability of this liquid crystalline phase to deform or adapt their TAG stacking to the interface curvature of the W/O emulsion (Nelis, Declercle, et al., 2019).

It has been observed that PGPR concentration has an effect on the rheological properties of DEs when the oil phase is crystallized, as the apparent shear viscosity rise significantly with crystallization. This behaviour could be associated to different factors, such as changes in polarity of the fat crystals when the surfactant molecules are adsorbed onto their surface (Ghosh et al., 2011), or due to partial coalescence, flocculation or aggregation of the oil droplets, or displacement of the high HLB surfactant by the excess of PGPR. PGPR also might hinder the

formation of a fat crystal shell in the primary emulsion, because it displaces the fat crystal themselves (Frasch-Melnik et al., 2010). However, AMF could form a fat crystal shell in the presence of PGPR (Nelis, Declercle, et al., 2019), which indicates that fat crystal shell formation is not well understood and needs further investigation.

#### 4. Rheological and tribological performance of double emulsions

The rheology of a food product is relevant to understand its flow behaviour, which determine its manufacturability and sensorial attributes (e.g. sensory thickness). Having knowledge of the rheological properties allows controlling the final properties of a food product (ingredients functionality), designing and evaluating their stability during processing conditions (e.g. transport phenomena in pipes) and correlate sensory data with textural properties. The properties of emulsions not only depend on the rheological properties of the individual components and the concentration of the dispersed phase, but also on the microstructure, e.g., the droplet size. For simple emulsions with a volume fraction higher than 0.64, all larger droplets experience transitions to shapes between spheres and polyhedra, and smaller droplets frequently occupy the interstices between large droplets. In general, these structures come about by the dynamic equilibrium between droplets breakage and coalescence (Bruyn et al., 2013; Leiva & Geffroy, 2018), which can be easily modified by an external stress field such as that imposed by a shearing flow. On the contrary, for diluted emulsions, the viscosity depends on the continuous phase, but not so much on the dispersed droplets (Tatar et al., 2017).

The close interactions between two droplets in DEs has an important effect on the evolution of the emulsion microstructure when a shear rate is applied. In the simplest of cases, two types of forces will govern the interaction between two colliding droplets: hydrodynamics forces and intermolecular forces. The hydrodynamic forces are mainly due to the viscous stress field, while the intermolecular forces are due to an extra interfacial energy, which is the result of van der Waals attraction, electrostatic repulsion, steric, or other type of forces. When two droplets collide or approach each other, the hydrodynamic and the intermolecular forces behave differently, e.g., (i) droplets bounce as elastic bodies; (ii) droplets flocculate; or (iii) droplets coalesce. Such processes happen depending on the droplet size, distribution and surfactant properties (Ivanov et al., 1999).

To the best of our knowledge, the rheological behavior of DEs is not well understood to date. The current research work focuses on enhancing the stabilization of DEs rather than understanding the relationship of the microstructure with the rheological properties. The major unresolved challenges that come up are: what is the contribution of the inner droplets to the rheology of the DEs? Does the type of internal structure (e.g., size, number of droplets, interfacial properties) of the DE have a significant effect on flow behaviour? Having a control of the size and number of inner droplets is relevant to understand their effect on the rheological properties of DEs. As discussed before, microfluidic technique might overcome this problem, as they allow to control the size and number of inner and outer droplets carefully (Choi et al., 2018).

Luo et al. (2017) studied the rheological behaviour of three different inner structures in DEs stabilized using lecithin and polymer surfactants; type I (several water droplets, but with vesicle form), type II (several water droplets) and type III (one single water droplet). The viscosity was different for each of them, being higher for those DEs prepared with lecithin at both interfaces. This might be associated to the vesicle structure of the DEs. Nevertheless, when Abil EM90 and the blend of lecithin with PEG-6 caprylic/capric triglyceride surfactant (as low and high HLB value, respectively) was used, the structure was a core-droplet (type III). The core-droplet structure showed lower viscosity than the vesicle structure, but equal viscosity to the Abil EM90/lecithin (as low and high HLB value, respectively), which presented a type II structure.

From modelling studies, it was also demonstrated that the viscosity

of the inner core water droplet (only one droplet entrapped in an oil droplet), changes the relative viscosity of the DEs, which also depended on the magnitude of the shear rate and the proximity of both interfaces (W/O and O/W). The higher the viscosity of the core-droplet, the lower the relative viscosity at low shear rates; but at higher shear rates the relative viscosity increases. This behaviour is the result of the inward flow along the water droplet interface originated by surface tension gradients (Marangoni flow), which causes resistance to droplet deformation (Choi et al., 2018). Nonetheless, the concentration of lecithin as surfactant of the secondary emulsion has an effect on the viscosity, being higher for emulsions with 1 wt% of lecithin. When the internal structure is lost, the viscosity decreases as the external droplets become smaller, which happens at higher values of lecithin (Tian et al., 2021). In addition, each type of emulsion presented different storage modulus ( $G'$ ) and loss modulus ( $G''$ ). At low strain, the  $G'$  was higher for lecithin/lecithin emulsions, while the  $G''$  was higher by using Abil EM90/lecithin (Luo et al., 2017). This suggests that lecithin/lecithin DEs have a more elastic behaviour, while the Abil EM90/lecithin presented a predominant viscous behaviour under shear stress.

Generally, DEs have shown a shear-thinning behaviour that might be associated to the deformation of the droplets, (Prichapan et al., 2021; Tian et al., 2021), which has also been predicted by numerical modelling (Choi et al., 2018). The presence of a blend of polysaccharides in the W<sub>1</sub>-XG + LBG phase modified the rheological behaviour of the prepared DE, which presented higher values of  $G'$  than W<sub>1</sub>-water and W<sub>1</sub>-XG (Tian et al., 2021) (Table 2). Similarly, the viscosity was higher in DEs stabilized with multiple coating (SA-CHI) at the interface of the external droplets (oil phase) than those DEs with one single coating (SA). For the latter, viscosity also depended on the concentration of CHI (values higher than 0.35 wt%) (Table 2). For a DE stabilized with  $\beta$ -cyclodextrin (Table 2), higher values of  $G'$  over  $G''$  was shown, with elasticity predominating over the viscous component. It was also found that the increment of  $G'$  was proportional to the amount of emulsifier, which suggests the presence of a strong solid-like network at the interface results in higher viscoelasticity of DEs (Eslami et al., 2017).

It is now well recognized that the sensorial perception of food products depends not only on rheological properties. The oral processing is a dynamic phenomenon that involves mixing with saliva, the food-saliva mixture acts as lubricant helping to swallow and transfer the food bolus to the stomach. For example, the enzymes of saliva, e.g.  $\alpha$ -amylase, may also affect the perception of the food; in fact, they reduce thickness during chewing by hydrolysis of starch when hydrophobically-modified starch is used as the emulsifying agent (Chen & Stokes, 2012; Stokes et al., 2013). Thus, tribology *i.e.* friction and lubrication properties of DEs depend not only on the formulation of DEs but also how the DEs interact with oral surfaces and thus, may affect the mouthfeel of DEs (Prakash et al., 2013; Sarkar et al., 2019; Sarkar & Krop, 2019; Sarkar et al., 2021). The composition of the food product affect both the rheological and tribological properties, which influence the final acceptance or rejection of the product by the consumers.

Lipid components provide characteristic sensorial attributes to high fat products, which make it difficult to reduce fats to make healthier options while conserving their intrinsic characteristics. As it can be seen in the list of patents filed in last few years (Table 6), there are limited examples of DE formulations being used in the industry to produce low fat products. Most of these recent patents focus on fat crystals as Pickering stabilizers. More importantly we need to understand the relation between the structural properties of DEs and their organoleptic properties. One of the functions of fat in food is to decrease the friction in the mouth and therefore provide the creaminess attribute. For simple O/W emulsions, the coalescence of the droplets during the oral process have shown increased fatty-perception (Dresselhuis et al., 2007; Fuhrmann et al., 2019; Torres et al., 2018). Also, to improve the lubrication performance, droplets should deform and/or coalesce to some degree during the dynamic process, thus, designing the structure and the ingredients to maintain certain deformations might enhance the

creaminess perception. Therefore, the ability of DEs to act as good lubricants relies on their capabilities to conserve their structure while the fat content is reduced, but coalesce under tribological stress to form a lubricating film.

In W/O/W emulsion, the oil droplets establish the properties of the system, and the presence of inner water droplets tend to modify the viscosity of the oil droplets, which is proportionally related to the concentration of the entrapped water. This increased viscosity will hinder the deformation of the droplets and therefore their ability to reduce the surface friction. In addition, the breakdown of the droplets, either during processing or during the oral process, might liberate water droplets to the continuous water phase (W<sub>2</sub>). The liberation of water might increase the friction, as water is a weak lubricant. However, if water contains a gelling agent as seen in the previous examples of DEs (Table 2, Fig. 4k and l), it might result in the formation of a hydrating film entrained between the oral surfaces reducing friction. In addition, the size of the droplets in DEs is normally higher than in simple emulsions (higher than 1  $\mu$ m) because of the presence of inner water. As the gap between the oral surfaces is much lower, the friction might be governed by the continuous W<sub>2</sub> or highly deformed W/O droplets entering the contact region.

To our knowledge, there has been only one study that has examined the tribological properties of DEs in a systematic manner (Oppermann et al., 2017). The authors found that the presence of PGPR enabled decreasing friction due to hydrophobic interaction between PGPR and the hydrophobic surfaces used in tribological experiments. However, increasing the volume fraction of inner water droplets or gelling of the inner water phase (W<sub>1</sub>) made the droplets less deformable, hindering entrainment and thus increased friction. This suggests that the formulation and microstructure of DEs not only affect their stability during storage but also their breakdown during oral processing and consequently might affect mouthfeel perception. Thus, rheology and tribological examination of DEs requires further research to understand its relationship with sensory attributes before DEs can be applied as fat replacers in real food systems.

## 5. Conclusions

In the food industry, DEs can be used as a promising microstructural approach to improve the nutritional profile of food products by either encapsulating more efficiently functional components (vitamins, antioxidants amount others) or decreasing the calorific content when a percentage of lipids is substituted with water. DEs have been used to design different types of cheese, meat systems, mayonnaise and dressings. The strategies used to improve the stability of DEs will depend on the desired characteristics and functionality of the final product. The loss of inner water during destabilization of fat-reduced products will change the external W<sub>2</sub> fraction and therefore the overall sensorial characteristic. Meanwhile, the release of sensitive components due to destabilization of DEs will decrease their nutraceutical-intended properties. Thus, special attention has to be taken to control the diffusion mechanisms during fabrication, storage and release. In the last few years, there has been progress in processing techniques such as microfluidics, which can enable one-step instead of conventional two-step processing of DEs.

Although a holy-grail solution to fully prevent diffusion in DEs is yet to be reported, some strategies such as the use of oleogels to gel the oil phase, hydrogels gelling the aqueous phases; Pickering particles (particles or core shell structures formed by fat crystals) and multiple coating layers formed by biopolymers have shown a remarkable promise in enhancing the stability of DEs. Although Pickering particles are showing an interesting trend in stabilization of DEs, the relative scarcity of food grade particles for stabilization of water-oil interfaces appears as a limiting factor when stabilizing DEs solely by particles. One promising approach can be to combine the use of particles (interfacial stabilization) and gelling of the bulk aqueous phases (bulk stabilization) to offer

**Table 6**  
List (non-exhaustive) of patents in fabrication of double emulsions.

Patent number	Patent name	Reference	Filing date	Example of applications
JP6002491B2	Method for producing double-emulsified oil/fat composition	Shida et al. (2012)	2012	Imparting an excellent flavor to foods with stable double emulsification (W/O/W or O/W/O)
CN112314714A	Pickering double emulsion with interface stabilized by solid fat and preparation and application thereof	(CN112314714A, 2020)	2020	Low-fat or low-fat-digestibility foods
BR112020023179A2	Food composition and method for preparing a food composition	Nieman et al. (2019)	2019	Reduced fat, spread-like product may further comprise ingredients typically found in spreads
JP2019505215A	Low fat seasonings, methods and products	Zhang et al. (2017)	2017	Seasoning like mayonnaise, creamy salad (e.g. Caesar) dressings, sauces, tartar sauce and sandwich spreads
20100233221	Stable double emulsions	Britta et al. (2010)	2010	Food products selected from salad dressing, mayonnaise-type products, sauces, spreads, soups, desserts, creams

ultrastability to DEs, which needs to be tested in the future. Although highly important in view of using DEs as fat replacers in food applications, the macroscopic properties of DEs such as rheology and tribology parameters have received relatively little attention in the literature to date. Tribological measurements has recently been used to link the structural properties of DEs to a qualitative measurement of the mouthfeel perception of food products. Future research in characterizing the material performance and sensorial properties of DEs are crucial to finally achieve fat replacement in food products using this promising microstructural approach, without compromising pleasurable attributes.

#### CRediT authorship contribution statement

**Elizabeth Tenorio-García:** Conceptualization, Methodology, Investigation, Writing – review & editing, Visualization, Writing – original draft, Writing – review & editing, Funding acquisition. **Andrea Araiza-Calahorra:** Conceptualization, Methodology, Writing – review & editing. **Elena Simone:** Conceptualization, Writing – review & editing, Supervision. **Anwasha Sarkar:** Conceptualization, Project administration, Writing – review & editing, Supervision.

#### Declaration of competing interest

None.

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