Review

Protein- and polysaccharide-based particles used for Pickering emulsion stabilisation

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ABSTRACT

A few protein- and polysaccharide-based particles can function as effective stabilisers in multi-phase food systems. Combining both polymer-based particles and tailoring the wettability of colloidal systems result in particle-stabilised emulsions with great stability. High internal phase emulsions (HIPEs) have also been produced using such particles giving rise to a more stable, highly viscous structure. Thus, the purpose here is to review the advantages and disadvantages of using protein, polysaccharide and protein-polysaccharide complexes and conjugates for stabilising emulsions, highlighting the composites of amphiphilic protein-polysaccharide particles that can function as outstanding copolymer stabilising agents. The current challenges and emerging research trends are exploring renewable, sustainable, clean-label, and eco-friendly biopolymer particles that are effective as Pickering stabilisers.

1. Introduction

The use of solid particles as stabilisers for oil droplets in water dates back over a century ago (Binks, 2002). The first studies documenting the particle-stabilised emulsions, also referred to as Pickering emulsions, were reported by Ramsden and Pickering and have had an increasing interest in recent years (Berton-Carabin & Schroën, 2015). Despite the theories on inorganic and synthetic polymer-based Pickering emulsions are well-established, research about the use of edible colloidal particles to stabilise emulsions is increasingly attractive (Xiao, Li, & Huang, 2016). The current challenges and emerging research trends address using renewable, sustainable, clean-label, and environmentally friendly biopolymer particles that are not only effective as Pickering stabilisers but are also acceptable as food-grade materials (Rayner et al., 2014).

In multi-phase food systems, protein and polysaccharide particles have the ability to function as stabilizers and thickening agents, either in the form of nano- or micro-particles (Dickinson, 2012). In addition to its surface activity, proteins have fast interfacial adsorption kinetics, whereas the polysaccharide moieties form a thick steric layer because they protrude into the aqueous phase providing electrostatic repulsive forces against droplet aggregation (Chen et al., 2018). Nevertheless, modification of the particles' surface hydrophobicity and also the formation of protein-polysaccharide complexes have been recommended in many cases, as protein particles may cause aggregation and structural instability in Pickering emulsions, and polysaccharide-based particles give poor emulsifying performance and surface activity (Ashaolu & Zhao, 2020).

Physical stability and textural characteristics of colloidal systems (dispersions, emulsions, foams, gels, and their mixed variants) in food manufacture can be improved using well-known and efficient methods of associative interactions between proteins and polysaccharides (Dickinson, 2017). There is a great diversity of possible interactions between these types of macromolecules, including non-covalent attractive forces such as electrostatic, hydrogen bonding, hydrophobic, and van der Waals. In addition, covalent bonds are mostly formed between side-chain-exposed functional groups resulting in an irreversible binding (Semenova, 2017).

Novel opportunities for the stabilisation of food emulsions using solid biopolymer nanoparticles and microparticles are emerging. The major advantage of such stabilisation is its longevity, regarding coalescence, with no significant structural change over storage. Due to the effective steric structural barrier formed by the adsorbed solid particles, only slight coarse droplets might be formed after several months (Dickinson, 2013; Semenova, 2017). However, a required dual

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wettability of the particles by oil and water is a critical factor for obtaining emulsions with long-term stability (Binks, 2002; Gao et al., 2014). Therefore, not all food biopolymers are suitable as Pickering stabilisers for emulsions due to the limited wettability and interfacial properties. As Sarkar and Dickinson (2020) explained in their latest work, it is important to define correctly the stabilisation mechanism to distinguish those cases where the particles are acting as genuine Pickering stabilizers, through direct monolayer adsorption at the liquid–liquid interface, from those cases where the particles are predominantly behaving as 'structuring agents' between droplets without necessarily adsorbing at the interface.

Regarding to the advances in the use of Pickering emulsions, gel-like emulsions obtained from Pickering systems are an emerging trend. In addition to the high physical stabilisation and oxidative stability due to a strong gel-like network, Pickering emulsion gels also represent a novelty for delivering bioactive compounds (Li, Zhang, Li, Fu, & Huang, 2020; Mao, Lu, Cui, Miao, & Gao, 2019). Moreover, biopolymeric particles have attracted increasing interest in stabilising emulsions with high volume fraction of internal phase, which are named as high internal phase emulsions (HIPEs) (Okuro, Martins, Vicente, & Cunha, 2020). Studies have reported that, in addition to be affected by the volume fraction of the dispersed phase, the rheological behaviour of HIPEs can be controlled by manipulating the particle properties and the particle interactions (Zou, van Baalen, Yang, & Scholten, 2018).

Despite the increasing number of studies on Pickering emulsions available in literature over the past few years, this review specifically summarizes the major advances that have occurred in the use of biopolymer-based particles for the stabilisation of emulsions. Special interest is directed to get better understanding of the underlying mechanisms of interfacial stabilisation by adsorbing biopolymer particles acting as actual Pickering stabilizers with a view to assisting the industry in formulating sustainable food emulsions offering improved food properties. Our review focusses on recently achieved insights concerning the contribution of proteins and polysaccharides and their associative interactions, considering different aspects: (i) The characterisation of micro and nanoparticles of the most common biopolymers (protein and polysaccharide) employed for emulsion stabilisation. (ii) The review and analysis of relevant studies about emulsion stabilisation using biopolymeric particles. (iii) The ongoing challenges and novel techniques to achieve and assess biopolymer associations. Table 1 provides a list of recent investigations regarding protein- and polysaccharide-based particles used for Pickering emulsion stabilisation.

2. Food-grade particles for emulsion stabilisation

2.1. Polysaccharide-based particles

Natural biopolymers, such as polysaccharides, can be an attractive source of particulate material for potential use in foods. Significant research has shown that modified starches, cellulose-based, and chitin-based particles could be used as Pickering stabilisers in food-grade emulsions (Table 1) (Dickinson, 2017; Murray, 2019).

Increasing storage stability can be achieved when small starch particles are used, as decreasing starch particle size decreases droplet size of Pickering emulsions. Therefore, different methods have been reported for producing starch nanoparticles and nanocrystals: acid hydrolysis, high pressure homogenisation, ultrasonication, reactive extrusion, γ-irradiation, steam jet cooking, nanoprecipitation, enzymatic debranching and recrystallisation, polyelectrolyte complex formation, electrospinning, electro spraying, and self-assembly (Sun, 2018; Zhu, 2019).

Modified starch particles of various biological sources play the major role as food-grade particles with potential to be used as Pickering stabilisers for oil-water (O/W) emulsions (Murray, 2019). Because these particles are generally highly hydrophilic, chemical modifications are required to make them more hydrophobic and confer higher affinity for the O/W interface (Berton-Carabin & Schroën, 2015). The particles remain intact even after the hydrophobic modification, thus presenting proper wettability by the aqueous phase and being able to be used as a stabiliser in Pickering emulsions (Song, Zheng, Ma, Kang, & Ren, 2020; Wang, Fu, Tang, Huang, & Zhang, 2017). Starch esterification with octenyl succinic anhydride (OSA) is the most widely used modification. It consists of a partial substitution of the hydroxyl groups by hydrophobic substituents to provide them an amphiphilic character and interfacial activity (Altuna, Herrera, & Foresti, 2018; Saari, Wahlgren, Rayner, Sjöö, & Matos, 2019; Wang, Luo, Chun-Chen, Xiong-Fu, & Tamer, 2020). It is important to highlight that in addition to the properties of the starch raw material, other factors may influence the physicochemical properties of OSA-modified starches: the processing conditions used not only during, but also before and after the modification in case pre-/post-treatments are applied; the extent of derivatisation; and the distribution of the introduced groups within the starch granules (Altuna et al., 2018). Other chemicals used to increase the hydrophobicity of starch granules include acetic anhydride and phthalic anhydride. However, starch particles produced using chemical modifications may not be appealing to consumers in the rising clean-label ingredients market (Zhu, 2019).

Another important group includes cellulose derivatives. Native cellulose is a hydrophilic polysaccharide lacking good emulsifying ability. However, studies have demonstrated that stable Pickering emulsions can be formed using various cellulose particulate materials which act as emulsifiers by adsorbing at the O/W interface (Kalashnikova, Bizot, Bertoncini, Cathala, & Capron, 2013; Tang, Sisler, Grishkewich, & Tam, 2017). Cellulose crystals with different shape and size can be produced by isolating crystalline zones by chemical, mechanical and/or biological techniques in order to develop several functional ingredients. Depending on the preparation methods and sources, examples include microcrystalline cellulose, microfibrillated cellulose, regenerated cellulose, nanocrystalline cellulose, nanofibrillated cellulose, and bacterial cellulose (Nsor-Atindana et al., 2017).

Among these particles, cellulose nanocrystals (CNCs) display the characteristics of unique nanostructure, amphiphilic nature, biocompatibility, low carbon footprint, chemical tenability, environmental sustainability, and anticipated low cost, leading to a growing popularity as emulsion stabiliers. CNCs are generally rod- or needle-shaped particles exhibiting a high crystallinity and a nanometer size with high aspect ratio. The properties of CNCs mainly depend on the cellulose sources and extraction processes and definitely influence its emulsification performance as Pickering stabilizers, especially the surface charge, wettability and size. The self-assembly of CNCs at the O/W interface form a steric barrier preventing the emulsion droplets against coalescence (Dai et al., 2020).

To date, many strategies have been applied to improve the emulsification performance of CNCs, by decreasing their surface hydrophilicity or increasing their hydrophobicity through a variety of physical and chemical modification. The electrostatic screening of charged groups on CNCs by the addition of salts is one of the simple but effective strategies in this regard. A simple surface modification with OSA remarkably improves the surface hydrophobicity of CNCs (Chen et al., 2018, 2018; Du Le, Loveday, Singh, & Sarkar, 2020), thus improving the emulsification performance of CNCs. Usually, Pickering emulsions stabilised by CNCs are prepared using shearing or sonication as emulsification technique (Chen, Liu, & Tang, 2019).

Besides cellulose derivatives, chitin nanoparticles represent another interesting group of biopolymers suitable for Pickering stabilisers. Chitin is a linear polysaccharide that works as a major structural component in the exoskeleton of various marine invertebrates. It is extracted from marine shell waste streams on an industrial level (Muxika, Etxabide, Uranga, Guerrero, & de la Caba, 2017). Chitin has garnered considerable interest due to its non-toxicity, biocompatibility, and biodegradability. To extend its applications, chitin has been converted into chitosan, chitin nanocrystals, chitin nanoparticles, and/or chitin nanofibers (Sun,

Table 1
Examples of Pickering emulsions stabilised by protein- and polysaccharide-based particles.

	Particle material	Dispersed/continuous phases	Homogenisation	Findings	Reference
Polysaccharides	Rice starch	Sunflower oil (50% v/v)/OSA-modified rice starch (1–2 wt%)	High speed homogenizer 11,000 r/min for 2 min	Starch particles and surfactants improved oxidative stability	Song et al. (2020)
	Waxy maize and waxy potato starches	Orange oil (5% w/w)/OSA-starch spherulites	High speed + high pressure homogenizer 150,000 rpm for 3 min	Retarded the lipid oxidation rate	Wang et al. (2017)
	Quinoa starch; waxy maize; oat starch	MCT (5 wt%)/starch in phosphate buffer (pH 7) (200–3200 mg/g oil)	High-shear mixer 22,000 rpm, for 1–5 min	Systems dominated by small granules at the interface were less affected by emulsification time	Saari et al. (2019)
	Bacterial cellulose (BC)	Dodecane (10–50 v%)/BCNFs suspensions (0.1–0.5 wt%)	High shear blender 10,000 rpm for 2 min	Strong inter-droplet network formation led to a gel-like behavior	Q. Li et al. (2019)
	Chitosan	Canola oil (0.2-.0.8 wt%)/ACPs (1.0 wt%) (pH 6.4–7.0)	Homogenized using a rotor/stator 12,000 rpm for 1 min	Generation of interconnected structures and gel formation.	Wang et al. (2020)
	Chitin	Corn oil (10% v/v)/Chitin nanocrystals (0.1, 0.5, 1 and 1.5% w/v)	Ultra-sonic homogenizer 2 min with 10-s intervals	Higher stability attributed to lower droplet sizes	Barkhordari and Fathi (2018)
	Rice starch	N-hexan (10–70%)/OSA-modified rice starch (OS-RS) (0.1–5%)	High-speed homogenizer 20,000 rpm for 1 min	Emulsion stability affected by distribution of OS groups related to the concentration of NaOH	Wang et al. (2020)
	Waxy maize starch	MCT (5%; w/w)/OSA-modified starch (200 mg/mL oil) in phosphate buffer (pH 7, 0.2 M NaCl)	Vortexing for 10 s and high-shear mixed at 22,000 rpm	Emulsion droplet size and stability affected by differences in starch particle size and molecular structure	Saari et al. (2019)
	Microcrystalline cellulose	Dodecane oil (10%, v/v)/CMCNa modified MCC composites (0.5–2% w/v in water)	Ultra turrax 12000 rpm for 3 min.	Stability attributed to the inter-droplet network formation	Ahsan et al. (2019)
	Nanofibrillated cellulose	Soybean oil + Vitamin D_3 (10% w/w)/NFC (1% w/w) in buffer solution (10 mM NaH_2PO, pH 7.0)	High-shear mixer for 2 min + high-pressure homogenizer at 12,000 psi for 3 cycles	The network of aggregated fibers slowed down lipid digestion	Winuprasith et al. (2018)
Proteins	Gliadin + WPI	Corn oil (30–70 wt%)/aqueous GNP solution (1% w/w)	High-shear mixer 12,000 rpm for 2 min	WPI addition could facilitate emulsion gel formation	Zhu, Chen, et al. (2018)
	Soybean protein isolate (SPI)	Soybean oil (10–30 wt%)/SPI microgel suspensions	Ultra-turrax 9,000 rpm for 2 min + high pressure or sonication (20 kHz, 400 W)	Stabilisation of O/W emulsions with low oil contents	Benetti et al. (2019)
	Soybean protein isolate (SPI)	Soy oil (20% v/v)/SPI-ACN complex dispersion	10,000 rpm for 2 min using Ultra-turrax	Protective effect on oxidative stability	Ju et al. (2020)
	Acid-soluble collagen	Algal oil (30% v/v)/collagen solution (0.01–1.5 wt%)	Ultrasound 10 min, 400 W	Gel-like structure with an increase in acid-soluble collagen concentration	Zhu et al. (2020)
	Gelatin nanoparticles	Fish oil (50% v/v)/gelatin nanoparticles solutions (0.2–4.0%)	Ultra turrax 11,500 rpm for 60 s	Creaming stability was dependent on the molecular structure, concentration, and form of the stabiliser	Ding et al. (2020)
	Zein nanoparticles	Cinnamon essential oil (12.5% w/w) + vegetal oil (37,5% w/w)/ZN solution	High shear homogenizer 12,000 rpm for 10 min	Effect in replacing 20% butter in cakes and extending the shelf-life	Feng et al. (2020)
	Pea protein microgel	Sunflower (20 wt%)/PPM dispersion (0.05–1.0 wt%)	Rotor-stator 8,000 rpm for 5 min	Ultra-stable droplets only at 1.0 wt % protein concentration	S. Zhang et al. (2020)
Protein-polysaccharide complexes	Okara dietary fiber + SPI	Soy oil (1:2 and 1:3)/ODF-SPI conjugates (5% w/v) dispersion	High-speed shear 20,000 rpm for 2 min	Maillard reaction time directly proportional to emulsion stability	Ashaolu and Zhao (2020)
	Chitin nanofibers + zein colloid particles	Soybean oil (20% w/w)/ChNFs-ZCPs complex dispersion	High-speed blending 12,000 rpm for 3 min	Oiling-off in the upper layer was avoided in the presence of ChNFs	Sun et al. (2019)
	Zein + Gum arabic	MCT (10–70 wt%)/ZGAPs (1% w/v) dispersions	High-speed homogenizer 12,000 rpm for 3 min	Long-term storage stability at oil fraction $\geq$ 50%	Dai et al. (2018)
	SPI + bacterial cellulose	Dodecane oil (20–50% v/v) SPI/TOBC (12.5:1) complexes dispersions	High-speed shear 16,000 rpm for 2 min	Better stability attributed to the increase in the complexes contents	X. Zhang et al. (2020)
	Gliadin + chitosan	Corn oil (50% v/v)/GCNPs dispersion	High-speed dispersive homogenizer 10 kr/min for 2 min	Retarding effects on lipid oxidation in emulsions stabilised by curcumin-loaded particles	M.F. Li et al. (2019)
HIPEs	Cellulose nanocrystals (CNCs)	Soy oil (80 wt%/OSA-modified CNCs (0.1–1.2 wt%)	High-speed shear 11,500 rpm	Stable and gel-like emulsions	Chen et al. (2018)
	Whey protein microgel	Corn oil (75% w/w)/WPM (0.5% w/w)	High-speed shear 17,000 rpm	Rigid layer around the oil droplets preventing coalescence	Zamani et al. (2018)
	Ovalbumin	Dodecane (10–92% w/w)/OVA dispersion (0,2–3,0 wt%)	High-speed shear 5,000 rpm for 2 min	Strong structural integrity and strong refolding ability	Xu et al. (2018)
	Soy β-conglycinin	Dodecane (10–89% wt%)/β-CG solubilized in phosphate buffer (pH 7.0) (0.08–1.0 wt%)	High-speed dispersing 5,000 rpm for 1 min	Stable upon heating and storage (60 days) but very prone to freeze-thawing	Xu et al. (2019)
	Bovine serum albumin	Dodecane (60–93% w/w)/gBSA particle solution	High-speed dispersing 5,000 rpm for 1 min	Stability corroborated by tendency of gBSA to form HIPE gels.	Xu et al. (2020a)
	Insoluble soybean polysaccharides		Ultra turrax 13,500 rpm for 60s.	Stability against storage and heating and reversibility of freeze-	Yang et al. (2020)

(*continued on next page*)

Table 1 (*continued*)

	Particle material	Dispersed/continuous phases	Homogenisation	Findings	Reference
		Soy oil (0.1–0.9 wt%)/ISP nanoparticles dispersions (0.125–1.5 wt%)		thawing-destabilization/re-emulsification	
	Chitin nanofibrils	Sunflower oil (66–88 wt%)/NCh suspension (0.5 wt%)	High-speed 22,000 rpm for 1 min	NCh forms a dense, connected network at the oil/water interface, preventing oil coalescence	Zhu et al. (2020)
	Citrus nanofibers	Avocado oil (75 wt%)/CNFs-TA suspensions	Ultra turrax 23,000 rpm for 3 min	Oxidative stability attributed to antioxidant interfacial shells around avocado oil droplets	Wang et al. (2018)

Octenyl succinic anhydride (OSA), Cellulose nanocrystals (CNCs), Soy protein isolate (SPI), Sodium stearate (SS), β-lactoglobulin (*β*-Lg), Bacterial cellulose nanofibrils (BCNFs), Aggregated chitosan particles (ACPs), Sodium carboxymethyl cellulose (CMCNa), Microcrystalline cellulose (MCC), Nanofibrillated cellulose (NFC), Anthocyanins (ACN), Chitin nanofibers + zein colloid particles (ChNFs-ZCPs), Okara dietary fiber + Soy protein isolate (ODF-SPI), Medium-chain triglyceride (MCT), Zein and gum arabic complex colloidal nanoparticles (ZGAPs), 2, 2, 6, 6-tetramethylpiperidine-1-oxyl radical (TEMPO), TEMPO-oxidized bacterial cellulose (TOBC), Whey protein isolate (WPI), High methoxyl pectin (HMP), κ-carrageenan (kC), Ovalbumin (OVA), Whey protein microgel (WPM), Soy *β*-conglycinin (*β*-CG), Bovine serum albumin (BSA), glycated BSA (gBSA), Insoluble soybean polysaccharides (ISP), Chitin nanofibrils (NCh), Citrus nanofibers (CNFs), Tannic acid (TA), Complex colloidal nanofibers (CNFs-TA).

Zhao, Liu, Li, & Li, 2019). Chitin nanocrystals and nanofibers exhibit good emulsifying ability and stability; they can be isolated from chitin extracts via chemical or physical methods and used to produce Pickering emulsions by adsorbing on the O/W interface. While chitin nanocrystals are generally prepared by acid hydrolysis, chitin nanofibers are prepared by partial deacetylation and physical grinding. Chitin nanofibers exhibit higher aspect ratio and higher content of cationic amino groups with better adsorption capacity and increased wettability at the interface, which improves emulsion stability (Barkhordari & Fathi, 2018; Zhu et al., 2020).

2.2. Protein-based particles

Proteins have long been recognised as excellent natural building blocks to prepare micro and nanoparticles due to their versatility in tuneable conformations (Xiao, Li, et al., 2016). Proteins good interfacial and emulsification activities are particularly the advantages to perform as suitable Pickering emulsions. Proteins stabilise emulsions not only by the creation of a physical barrier but also by the presence of repulsive steric and electrostatic interactions between the oil droplets (Tavernier, Wijaya, Van der Meeren, Dewettinck, & Patel, 2016). However, when proteins are adsorbed at the interface, they tend to suffer a structural unfolding, lateral attractive interactions between adsorbed proteins, and even denaturation and aggregation. Protein particles will require solid structural integrity which will prevent disruption or fully unfolding when adsorbed at the interface of droplets (Tang, 2020).

As a globular protein is heated, aggregates with varied morphologies may arise depending on the protein concentration and thermal conditions. As a consequence, it can generate spherical particles, flexible or rigid fibrils, and fractal clusters (Nicolai & Durand, 2013). Different kinds of protein-based particles have been reported to successfully stabilise O/W emulsions by the Pickering method (Table 1). The main protein-based particles can be classified according to their source; from plant origin (zein, kafirin, gliadin, soy and pea protein) and animal origin (gelatin, dairy protein such as whey protein, bovine lactoglobulin, bovine serum albumin, α-lactalbumin, and lactoferrin).

Proteins from plant sources exhibit an excellent Pickering stabilisation. In general, the emulsifying properties of plant proteins depend on their amino acid composition, pH, concentration, and lipid content in the resulting emulsion (Liang & Tang, 2014). Prolamins are plant storage proteins with potential application as O/W stabilisers as they are naturally insoluble in water and are hydrophobic. The hydrophobicity of prolamin particles can be modulated in combination with water-soluble polymers, which leads to good stabilisation (Murray, 2019). Regarding their stabilisation ability, zein from maize (Kasaai, 2018), gliadins from wheat (Zhu, Chen, McClements, Zou, & Liu, 2018), and kafirin from sorghum have been studied extensively (Xiao et al., 2015; Xiao, Lu, & Huang, 2017; Xiao, Wang, Pérez González, & Huang, 2016).

Zein is the major storage protein in maize and is an environmentally friendly material, recognised as safe for food applications (Weissmueller, Lu, Hurley, & Prud'Homme, 2016). Zein has a significant amount of non-polar amino acids (about 50% of total amino acids including leucine, alanine, and proline) and can form relatively hydrophobic nanoparticles due to its self-assemble capability (Kasaai, 2018; Wang & Padua, 2012). Moreover, zein-based complex particles, e.g. zein-polysaccharides and zein-polyphenols, have been successfully prepared via an antisolvent approach, which provides the self-assembly behaviour and changes the interfacial wettability, thus forming different stable zein-based complexes that could be used at the droplet interface in Pickering emulsions (Sun et al., 2019; Wang et al., 2015).

Kafirin, a sorghum protein, belongs to the prolamin family with the highest hydrophobicity – which makes them insoluble in water and soluble in alcohol. Although it resembles zein in its solubility, molecular weight, amino acid composition, and structure of polypeptides, kafirin is more hydrophobic than zein (Xiao, Wang, et al., 2016). It enables the production of more stable films with better gas and water vapour barrier characteristics (Xiao et al., 2015).

Self-assembled structure can be also found in gliadins – the major constituent of wheat protein. The nanoparticles that result from this natural process are due to both hydrophobic and hydrophilic regions on gliadin surface that support Pickering stabilisation (Zhu et al., 2018). In addition, intramolecular and intermolecular disulphide bonds may be formed by the numerous residues of cysteine in the chain. O/W emulsions and Pickering HIPEs have shown to be effectively stabilised by gliadin colloidal particles, giving rise to edible and biocompatible systems based on natural renewable resources (Hu et al., 2016).

Legume proteins are also among the plant proteins of great interest for the food industry. In addition to their widespread abundance and good functional attributes, they are low cost, sustainable, and impact customer perceptions in a positive way. Designing pea protein-based particles to stabilise Pickering emulsion droplets is gaining attention. The gelation properties of pea proteins have been extensively studied; these studies address limitations on the use of emulsions prepared with these protein particles due to the pH (Liang & Tang, 2014; Shao et al., 2015). However, pea protein microgels can be used to stabilise Pickering emulsions against coalescence over a wider range of pH and ionic strengths (S. Zhang, Holmes, Ettelaie, & Sarkar, 2020).

The fabrication of different nanostructures of soy proteins have been widely studied, evidences have fast accumulated to indicate that soy proteins are excellent building materials. Soy protein isolate is produced by a conventional process that consists of an alkali extraction followed by an acid precipitation. O/W emulsions are efficiently stabilised due to amphipathic nature of soy particles, which allows them to diffuse and to be adsorbed at the interface of oil droplets (Tang et al., 2017). Although

most proteins in soy protein isolate are in an aggregated state, nanostructured particles can be obtained if an appropriate pre-treatment is applied, e.g., shearing homogenisation, ultrasonication, or micro fluidisation (Benetti, do Prado Silva, & Nicoletti, 2019; Tang, 2019).

Concerning animal protein, gelatin is the denaturation product of collagen under different conditions (e.g., the action of acid, alkali, enzyme, or high temperature). Collagen is commonly found in animal products and by-products, as skin, bones and tendons. Gelatin is cheap, easy to obtain, and theoretically suitable for preparing Pickering soft particles because of its good gelling properties. However, due to its strong hydrophilicity and thermal dissolution, gelatin nanoparticles able to stabilise Pickering emulsions are difficult to obtain (Feng et al., 2019; Jin et al., 2017). Furthermore, taking into account that insects are a promising alternative for meat-like products, recent studies have shown comparable properties of cricket flours and protein isolates regarding emulsifying activity and foaming capabilities of legume flours (Stone, Tanaka, & Nickerson, 2019; Zielińska, Karaś, & Baraniak, 2018).

Dairy protein fractions, as whey proteins and caseins, are the major natural food emulsifiers, but there is a scarcity of reports on their application in Pickering emulsions (Destribats, Rouvet, Gehin-Delval, Schmitt, & Binks, 2014). Specifically, isolated globular proteins (e.g. β-lactoglobulin) denatured under specific conditions of pH and temperature have been used to prepare well-defined particles with emulsion stabilising ability (Su et al., 2020). However, dairy proteins are a chemically interesting source for emulsion stabilisation due to their ability to turn into protein microgels.

Microgels are deformable and soft polymer-based particles that, in contrast to an individual macromolecular species, possess a more complex structure and functionality acting as an emulsifier, thickener, or steric stabiliser. They are colloidal entities with definite particle-like features, and comprise a crosslinked network of polymer molecules. Their particular features enable the microgel particle to rapidly and reversible swell and deswell in response to various external stimuli, including changes in pH, temperature, ionic strength, as well as following the addition of cosolvents, polymers, and surfactants. They are surface active and the emulsion stability is attributable to the thickness, coherence, and elasticity of the adsorbed layer. Although many food proteins and polysaccharides can form edible microgel ingredients, such as casein micelles, whey proteins, legume proteins, and even starch granules (Dickinson, 2015), there are many challenges for the use of globular proteins as a kind of soft particles for stabilising Pickering emulsions. A strong intermolecular integrity has been recently reported by Tang (2020) as the common structural feature that allows globular proteins to act as soft particles with the required functionality for Pickering stabilisation. This author stated that the maintenance of this structural integrity can ensure the particle packing and arrangement relatively intact when they are adsorbed at the droplet interface.

2.3. Protein-polysaccharide complexes

Proteins can interact with polysaccharides through a variety of physical or chemical mechanisms, making them to assemble into structures that will provide new functionalities. Such combined particles have been currently applied as encapsulation and delivery systems, texturizing agents, fat replacers and as fiber- or film-forming structures. Designing biopolymer particles with specific properties requires to control the spatial organization of the different components, and also the nature of the molecular interactions acting between the components (Jones & McClements, 2010b). In addition, processing operations such as thermal treatment, mechanical stressing, crosslinking and pressurization have been reported by Weiss, Salminen, Moll, and Schmitt (2019) to generate bulk protein-polysaccharide matrices with improved functional properties.

Proteins and polysaccharides can associate with each other under conditions of opposed electrical charge. Proteins possess a net negative charge above their isoelectric point (pI) and a net positive charge below this pH. Proteins that possess a high net negative charge (pH > pI) have a repulsive force against anionic polysaccharides. However, when the pH is adjusted to around the pI of the protein (pH ≅ pI), localised cationic segments on the protein interact attractively with anionic groups on the polysaccharide leading to weak electrostatic complexation. Further pH reduction (pH < pI) induces greater interaction between the protein and polysaccharide, eventually resulting in phase separation of the fully neutralised complex, which is also termed a coacervate (Fig. 1). Complex coacervation is the association of the initially soluble protein-polysaccharide complexes into solid larger particles (coacervates) generally by reducing pH beyond the pI of the protein. This process results from both entropic and enthalpic factors and depends on compositional and environmental variables, such as polymer type, pH, temperature, and ionic strength (Jones & McClements, 2010a; Wu & McClements, 2015).

An alternative electrostatic particle formation mechanism involves the controlled heating of protein alone or even of protein-polysaccharides mixtures, since the globular protein in protein–polysaccharide complexes tend to denature and aggregate by a fairly similar mechanism to globular protein alone at higher temperatures (Jones & McClements, 2010a). A pH adjustment is required to coat the protein nanoparticles with polysaccharides (Fig. 1). Hence, biopolymer nanoparticles are formed when the protein is heated above its thermal denaturation temperature, following by electrostatic interaction with a polysaccharide at a pH close to the protein's pI. The nucleation and growth of the biopolymer particles can be managed by controlling conditions such as temperature, time, concentration, pH, and ionic strength, giving rise to different nanoparticle sizes (Dickinson, 2015; Jones & McClements, 2010a; Xiao, Li, et al., 2016).

These stable inter-biopolymer electrostatic solid complexes are generally known to form and stabilise emulsions effectively, although many parameters including salt concentration, pH values, and protein to polysaccharide ratio can influence the protein-polysaccharide interaction. Consequently, it is convenient to covalently cross-link the biopolymers within the particles in order to increase their stability. Cross-linking can be carried out by two main ways: using chemical (Maillard reaction) or enzymatic approaches depending on the specific characteristics of the involved biopolymers (Chen et al., 2018; Jones & McClements, 2010b). Maillard reaction can be used to cross-link proteins and polysaccharides within the biopolymer particles formed by spray- or freeze-drying. After preparing the biopolymer particles by drying, the system can then be subjected to dry-heating and promote the Maillard reaction. Protein-polysaccharide conjugates can also be produced by enzymatic methods. Using enzymes to structure foods is an ecologically and economically viable alternative. Laccase-induced biopolymer conjugation through crosslinking reaction, for example, has shown great potential to improve the stability of gelatin-pectin microgel particles and also to enhance the functionality of colloidal foods, including the prevention of emulsion coalescence and modulation of encapsulated bioactive compounds release (Jones & McClements, 2010b; Zeeb, McClements, & Weiss, 2017).

3. Pickering emulsions

3.1. Pickering emulsions with polysaccharides

Native starch granules have been susceptible to chemical and physical modifications to become suitable for producing Pickering emulsions (Zhu, 2019). Wang et al. (2020) prepared OSA-modified rice starches with the same degree of substitution using different percentages of sodium hydroxide (NaOH) as catalyst. The storage stability of Pickering emulsions formulated by OSA-modified starch particles was greatly affected by the OSA group's distribution, which was related to NaOH concentration. The results indicated that high concentration of NaOH affected the structure of starch granules and induced OSA groups to distribute more uniformly in the granule. Rheological analysis indicated

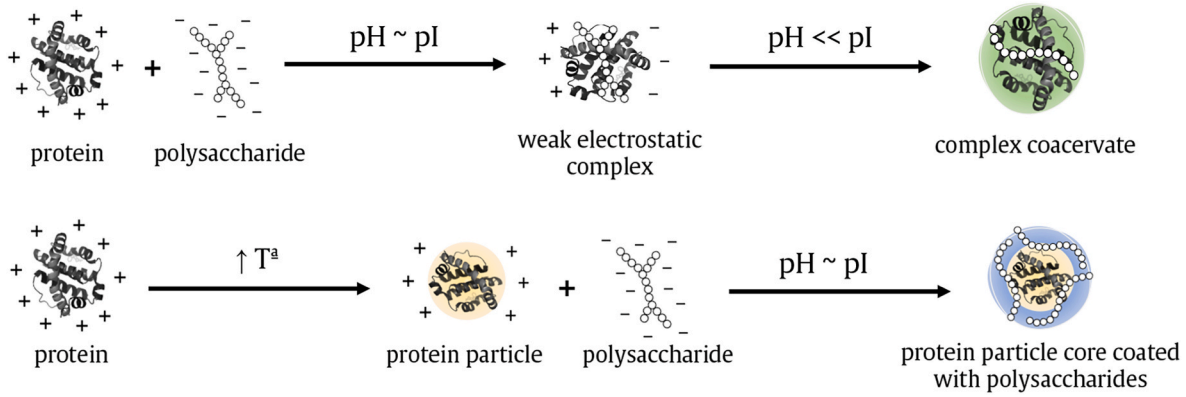

Fig. 1. Schematic representation of both protein-polysaccharide non-covalent interactions.

that these Pickering emulsions displayed good shear stability with shear-thinning behaviour, as the high viscosities at initial low shear stress decreased gradually and linearly with increasing shear rate. The authors suggested that the modified rice starches led to formation of a weak droplet network structure in the emulsion that was oriented in the flow direction, offering less resistance to flow. Thus, OS-starch provided a novel particle stabiliser for improving the rheological properties of Pickering emulsions.

Saari et al. (2019) investigated the stability of emulsions prepared by OSA-modified waxy maize starch in three different forms: granules, dissolved starch, and non-solvent precipitated starch as Pickering stabiliser. Non-solvent precipitates were obtained through ethanol precipitation of dissolved waxy maize. The varied sizes and shapes of the waxy maize-based emulsifiers influenced the resulting emulsion droplet size and stability. Optimum emulsifying properties based on droplet size, size distribution microscopic images and stability were obtained with the non-solvent precipitates, which allowed the emulsions to remain stable after one year of storage. Thus, this study showed the high potentiality of non-solvent precipitated starch as Pickering stabiliser.

Sánchez de la Concha, Agama-Acevedo, Aguirre-Cruz, Bello-Pérez, and Álvarez-Ramírez (2020) compared the emulsification capacity of waxy maize and amaranth starch nanocrystals chemically modified with OSA. OSA treatment modified the structure of nanocrystals by conferring superficial charge, which increased the repulsion forces between oil droplets incorporated with nanocrystals. Amaranth starch nanocrystals exhibited superior emulsification ability than waxy maize starch nanocrystals. The authors reported a feasible alternative to stabilise O/W emulsions by using a combination of nanocrystals and OSA treatment. The results in this study showed that the combination of nanocrystals and OSA treatment is a relatively simple and effective approach for stabilisation of O/W emulsions.

Song et al. (2020) fabricated sunflower O/W Pickering emulsions using OSA-modified starch particles and small molecular surfactants as stabilisers. Authors showed that starch particles were compatible with anionic surfactants such as sodium dodecyl sulphate and could improve the stability of Pickering emulsions. Droplet sizes of emulsions stabilised by starch particles and surfactants decreased greatly compared to those only with starch particles. Particle-stabilisers combined with anionic surfactants have the potential to enhance the stability in some commercial applications.

Research on cellulosic particles is considered as a promising alternative for surfactant-based systems on account of their non-toxicity, safety, biodegradability, and sustainability. The physicochemical properties, which define the functionality of microcrystalline cellulose, are determined by both the raw material and the preparation technique. Modified microcrystalline celluloses can be prepared by surface modification through polymer adsorption using no organic or harmful solvents. The polymer adsorption of sodium carboxy methyl cellulose on microcrystalline cellulose provided an important green method for potential use in the fabrication of eco-friendly Pickering emulsions (Ahsan, Zhang, Li, Li, & Liu, 2019).

Surface charges of nanocelluloses can tailor the wettability of these fine particles, playing a key role in the stability of the emulsions. Different crystalline allomorphs result in differences in properties of cellulose nanocrystals, such as their morphology, crystal structure, degree of hydrogen bonding, surface potential, and thermal and dispersion stability (Gong, Li, Xu, Xiang, & Mo, 2017). Li et al. (2018) obtained two nanocelluloses with different crystalline allomorphs prepared by sulfuric acid hydrolysis. The performance of crystalline nanocelluloses-I (CNCs–I; needle-like particles) to stabilise Pickering emulsions was better than crystalline nanocelluloses-II (CNCs-II; ellipsoid-shape particle). Pickering emulsions stabilised by CNCs–I presented droplet sizes about two times smaller and were more stable than CNCs-II after centrifugation. Therefore, authors concluded that the different effects on Pickering emulsions stabilisation were attributed to the difference of hydrophilicity and morphologies from different crystalline allomorph of CNCs.

Nanofibrillated cellulose has partially disintegrated nanofibril with the lateral dimensions in nanometer scale and lengths of several micrometres. Its properties are similar to that of crystalline nanocelluloses and make it able to be used as a thickener or emulsifier in food technology (Grishkewich, Mohammed, Tang, & Tam, 2017). Winuprasith et al. (2018) and Mitbumrung, Suphantharika, McClements, and Winuprasith (2019) encapsulated vitamin D3 within O/W Pickering emulsions stabilised by nanofibrillated cellulose, and reported it as an effective Pickering emulsifier while protecting the vitamin D3 from environmental stresses. This effect was attributed to its capacity to form a thick interfacial coating around the oil droplets, which provided strong steric and electrostatic stabilisation. The non-adsorbed nanofibrillated cellulose increased the viscosity of the continuous phase and gave rise to a network of oil droplets which improved the stability of emulsion.

Another potential cellulose derived stabiliser is bacterial cellulose. The supramolecular structure of bacterial cellulose nanosized fibrils (BCNFs) can be altered through mechanical treatment. Li et al. (2019) used high pressure homogenisation to modulate the morphology and size of bacterial cellulose. The content and particle size of the BCNFs had significant influence on the O/W interface, being associated with the strengthened intermolecular crosslinking and the increased steric barrier. The physical modification process can provide an easy green method for fabricating a potential BCNFs-based eco-friendly food-grade stabiliser for Pickering emulsion production.

In addition to cellulose-based particles, crystalline parts of chitin can be obtained by chemical or physical treatments, and chitin nanocrystals can be used to encapsulate and produce Pickering emulsions. Barkhordari and Fathi (2018) obtained chitin nanocrystals by hydrolysing chitin from prawn shells and used them in the Pickering emulsions

formulation. The developed nanocrystals were biodegradable and biocompatible ingredients that could be used for producing stable Pickering emulsions during four weeks of storage. The results showed that the mean diameter of oil droplets in the nanoparticle stabilised emulsion was smaller than in a lecithin containing emulsion with the same concentration (4.5 versus 10.9 μm, respectively). Kaku, Fujisawa, Saito, and Isogai (2020) and Zhang et al. (2015) also prepared chitin nanofibers with diameters around 50 nm, which formed stable Pickering emulsions through a simple dissolution and regeneration process. Hirsch, Cho, Kim, and Jones (2019) determined the interfacial and emulsifying properties of ground cricket-derived particles and only the smallest of the milled chitin particles were useful for emulsification, limiting their availability as industrial emulsifiers.

Highly charged chitin nanoparticles of three different average aspect ratios (≈5, 25, and >60 nm) were obtained using low-energy deconstruction of partially deacetylated chitin. Bai et al. (2019) observed that these nanoparticles were effective at reducing the interfacial tension and stabilised the O/W interface via network formation, thus becoming effective at stabilising Pickering systems, depending on the nanoparticles size, composition, and formulation. In addition, an increase in the interfacial wettability could have occurred from a deacetylation process before chitin transformation into the nanoparticles, enabling high electro-steric stabilisation. Then, the nanoparticle's surface coverage on the oil droplets as well as their ratio and long-term stability against coalescence can be easily controlled. Thus, a partial deacetylation of chitin particles would be a potential mean to improve interfacial characteristics of the chitin fraction and increase hydrophilicity.

Chitosan, in turn, is a highly hydrophilic biopolymer and requires surface modification or complexation with other polymers to improve its emulsification properties. Ribeiro, Borreani et al. (2020) investigated the ability of nanoparticles obtained by chitosan deprotonation or by ionic crosslinking to produce emulsions with different lipid phase fractions. Better droplet stabilisation was achieved using the deprotonation method when lower oil content was used. Chitosan nanoparticles could adsorb onto oil droplet surfaces, providing efficiency in encapsulating and protecting bioactive compounds. Moreover, deprotonated chitosan was able to create a three-dimensional network that entrapped the oil droplets while the crosslinked nanoparticles stabilised oil droplets along the continuous phase (Ribeiro, de Barros-Alexandrino et al., 2020) (Fig. 2).

Complexation of chitosan with other biopolymers is considered as an easy alternative to the currently used chemical surface modification

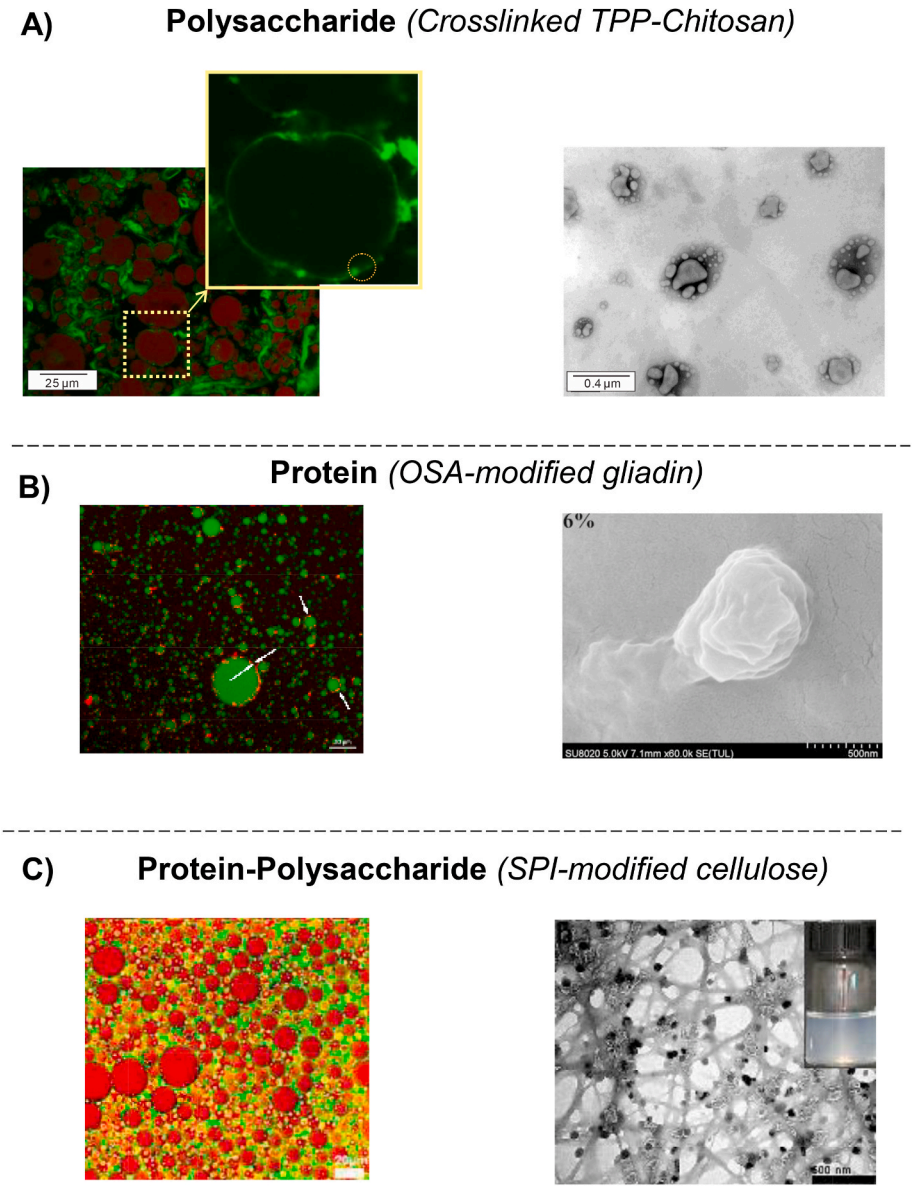

Fig. 2. Microscopic images of protein- and polysaccharide-based particles and their positions at the interface of the emulsion droplet. A) Confocal laser scanning microscope (CLSM) image of emulsions stabilised by crosslinked sodium tripolyphosphate (TPP)-chitosan particles and TEM image of the particles (Ribeiro, de Barros-Alexandrino et al., 2020); B) CLSM image of the Pickering emulsion stabilised by OSA-modified gliadin nanoparticle and scanning electron microscope (SEM) image of a gliadin nanoparticle with 6% of OSA content (X. M. Li et al., 2019); C) CLSM image of emulsion stabilised by SPI-bacterial cellulose complex and TEM image of the particles (X. Zhang et al., 2020).

strategies. Atarian, Rajaei, Tabatabaei, Mohsenifar, and Bodaghi (2019) prepared different Pickering emulsions stabilised with different chitosan and stearic acid ratios, and at different pH values. More stable emulsions were obtained using chitosan-stearic acid nanogels with higher stearic acid to chitosan ratios and at alkaline pH.

Chitosan and gum arabic nanoparticles have been synthesised and their use as novel stabilisers for Pickering emulsions was tested by Sharkawy, Barreiro, and Rodrigues (2019). Gum arabic, with its hydrophobic moieties, had an important function in modifying the wettability of the obtained particles. The nanoparticles formed an effective layer around the oil droplets, which prevented droplets from coalescence and assured the stability of emulsion. Moreover, the gravitational separation on long-term storage has been inhibited by increasing the oil volume fraction and the concentration of nanoparticles in the Pickering emulsions.

3.2. Pickering emulsions with proteins

The stabilisation of Pickering emulsions using protein particles usually requires physical and chemical modifications of the protein. Since there are limitations in using protein particles to stabilise Pickering emulsions as aggregation and structural instability, a good dual wettability is required to allow them to act as Pickering stabiliser. Water insoluble proteins such as prolamins have been used as a platform for water continuous emulsion stabilisation (De Folter, Van Ruijven, & Velikov, 2012; Donsì, Voudouris, Veen, & Velikov, 2017), however, most prolamins studies involve modification of the protein or association with other molecules. The use of zein specifically involves complexing the protein with a more water-soluble polysaccharide (Dai, Sun, Wei, Mao, & Gao, 2018), or with a second protein (Zhu, Chen, McClements, Zou, & Liu, 2018), or with an organic acid (Zou, Yang, & Scholten, 2018) to aid its dispersion in water and therefore adsorption at the O/W interface.

Rutkevičius, Allred, Velev, and Velikov (2018) showed that zein particles can stabilise W/O emulsions to a limited extent due to its high hydrophobicity. However, an addition of co-emulsifiers or a modification of zein particles with other surfactants allowed additional water incorporation into the emulsions and extended the stabilisation performance. The results indicated that adjustments prior to emulsification are required to provide zein particles with stabilising functionality to form W/O Pickering emulsions.

X.M. Li et al. (2019) prepared O/W Pickering emulsions stabilised by OSA modified gliadin nanoparticles, which were obtained through a facile anti-solvent precipitation procedure. The OSA-modified gliadin nanoparticles were used to improve the emulsification efficiency and emulsion stability, mainly at higher nanoparticle concentration and lower pH value with higher electrostatic repulsion (Fig. 2). The good storage stability can be attributed to the densely packed adsorption layer achieved by these particles on the oil droplet surface. At the same time this layer represents an interesting alternative to stabilise Pickering emulsions, and it could enrich the protein content in food products.

Liu, Liu, Guo, Yin, and Yang (2017) established a novel technology to construct structured algal oil products with no thermal or chemical treatment. Crosslinking was initiated by hydrophobic interaction under mild alkaline conditions, and interfacial disulphide crosslinking of gliadins was triggered by microfluidisation. The interfacial covalent crosslinking of these high stable emulsions can contribute positively to withstand environmental stress and provide the formation of a new class of food products.

Although gliadin and zein are both cereal prolamins, gliadin is relatively more hydrophilic than zein. X. Liu, Huang, Chen, Deng, and Yang (2019) synthesised zein-gliadin complex particles (ZGCP) using an antisolvent approach and investigated their efficiency as stabilisers to fabricate Pickering emulsions. Adding gliadin affected the self-assembly, aggregation, and wettability of ZGCP. These particles form a dense interfacial layer around droplet and have smaller droplet sizes than those obtained by zein or gliadin. Thus, ZGCP-stabilised emulsions demonstrated higher viscoelastic attributes and much better stability against coalescence.

Xiao et al. (2015, 2017) and Xiao, Wang et al. (2016) reported the first attempt of using the major prolamin from sorghum, kafirin, as a fully natural Pickering emulsion stabiliser. Kafirin was fabricated into spherical nanoparticles using antisolvent precipitation and was introduced as stabiliser for Pickering emulsions. The kafirin nanoparticles exhibited water over oil wetting preference, and the resultant Pickering emulsion manifested its superiority in storage and exhibited resistance against coalescence.

Most proteins in soy protein isolate are in the aggregated state, and with the appropriate pre-treatment, e.g. heat-induced aggregation, the aggregated state can be transformed into nanostructured particles (Tang, 2019). In a series of studies, Liu and Tang (2013, 2014, 2016, 2016, 2016) demonstrated that a heat treatment (above protein denaturation temperatures) of soy proteins can readily transform them into effective Pickering nanoparticle stabilisers for O/W emulsions. The heating remarkably strengthens the intraparticle interactive forces, and the internal structure of these heat-induced nanoparticles is mainly maintained by both hydrophobic interactions and disulphide bonds. Zhu, Zhang, Lin, and Tang (2017) evaluated the freeze-thaw stability of Pickering emulsions stabilised by nanoparticles from heated soy protein isolate and whey protein regarding flocculation, coalescence, and creaming index. The enhanced freeze-thaw stability of these emulsions seemed to be a consequence of the Pickering steric stabilisation, and the gel-like network formation. Soy protein isolate microgel particles produced by heat denaturation, followed by high pressure homogenisation or sonication, with different NaCl contents, could stabilise O/W emulsions by acting as a wall material for microencapsulating soybean oil by spray drying (Benetti et al., 2019). The presence of NaCl slightly affected the droplet size of the emulsions but led to an increase in flocculation and induced shear-thinning behaviour in the system. Spherical microcapsules with high oil retention (>80%) could be produced by spray drying the emulsions.

Ju et al. (2020) fabricated a novel Pickering emulsion stabilised by covalently bonded soy protein isolate-anthocyanin nanoparticles. The improved oxidative stability, resistance to *in vitro* digestion and noticeable emulsion stability reported in this study could be attributed to the intrinsic properties of Pickering emulsions.

The investigation of biopolymer-based microgels as potential stabilisers in Pickering emulsions offers new opportunities for food technologists. S. Zhang et al. (2020) designed pea protein-based microgel particles to create Pickering emulsions. Adjusting the pH of the emulsions to pI made the pea protein microgels adsorbed at the interface to aggregate, providing a higher degree of adsorption and enhanced interdroplet flocculation with shear-thinning character. Findings from this study provide opportunities for applying this protein microgels in food products, focusing on the growing demand by plant-based sustainable stabilisers.

Regarding animal protein, Chevallier et al. (2019, 2018) showed that it is possible to prepare heat-stable emulsions by using whey protein microgels and a sufficient number of caseins to fully cover a fat droplet surface. Whey protein microgels were highly stable against heating and are able to produce Pickering-like emulsions with long-term resistance to coalescence. However, the heat stability was reported to depend on the emulsion characteristics (concentration and presence of non-microgel proteins such as caseins). When compared to other polymers used for microgel production, whey protein does not require additional crosslinking agents (Schmitt et al., 2010).

Fibrillar proteins could also interact with polyphenols improving its emulsifying properties. Su et al. (2020) prepared composite nanoparticles with antioxidant capacity using β-lactoglobulin nanoparticles and epigallocatechin-3-gallate (EGCG) and applied them as Pickering emulsifiers to stabilise a model lutein emulsion. Forming composites between β-lactoglobulin and EGCG was due to the hydrogen bonds and

hydrophobic effects. β-lactoglobulin-EGCG composite nanoparticles exhibited stronger antioxidant activity and can exert their effects as particulate emulsifiers with partial wettability, which can produce a thicker interfacial layer around the droplets and repel the aggregation of the droplets through steric repulsion.

Gelatin particles, including microgels and gelatin-containing nanocomplexes, have been also reported to fabricate Pickering emulsions. However, few studies address their feasibility, as the unstable structure and potential toxicity of glutaraldehyde and acetone used to obtain rigid microspheres can limit their usage in edible Pickering emulsions (Zhu, Li, Li, & Wang, 2020). Ding et al. (2019, 2020) successfully prepared a crosslinked gelatin nanoparticle with good layer formation ability using a two-step desolvation method from bovine bone gelatin granules and used them to prepare Pickering emulsions. The authors explored the variables of the preparation method and storage temperature on the microencapsulation of fish oil by crosslinked gelatin nanoparticles in Pickering emulsions. The results demonstrated that gelatin molecular structure affected droplet size and creaming stability, but not the droplet shape. Another work by Feng et al. (2019) also prepared food-grade gelatin nanoparticles (GNPs) using a two-step desolvation method to stabilise O/W Pickering emulsion. The results showed that GNPs with narrow size distribution and good dispersion could only be obtained at pH 12. The Pickering emulsions stabilised by the GNPs had good uniformity and stability, with no obvious phase separation even after 30 days of storage – highlighting their potential to be used as food-grade Pickering stabilizers.

Zhu et al. (2020) assessed the feasibility of using acid-soluble collagen as a stabiliser to fabricate O/W Pickering emulsions. The stability of Pickering emulsions was enhanced as the acid-soluble collagen concentrations increased. A diminution of particle size and a gel-like structure formed in the emulsion is the main reason that enables an effective adsorption of acid-soluble collagen at O/W interface. Its mechanical properties have showed suitable to prepare viscoelastic emulsions with solid-like appearance and then to design reduced-fat products as breads and chocolates. However, factors such as the risk of pathogen contamination, cultural dietary, and price are the main limiting reasons to be overcome for real application of animal-based protein particles in food industries.

3.3. Pickering emulsions with protein-polysaccharide complexes

An additional interesting approach for producing Pickering emulsifier candidates involves the utilisation of protein-polysaccharide complex-based nanoparticles (Table 1). As shown in the current review improving the surface activities of polysaccharide-based particles is a prerequisite to reach the strong steric stabilisation. On the other hand, advantages of both protein and polysaccharide particles are shared when they are interconnected to form Pickering emulsions. These complexes are perfect to create distinct types of colloidal systems with unique properties that result in higher stability than using individual biopolymers. Complexes of zein with different polysaccharides have been used by several authors. Sun et al. (2019) produced stable Pickering emulsions using spherical zein colloid particles and fibrous chitin nanofiber complexes as stabilisers. Zein colloid particles were easily constructed by anti-solvent method and chitin nanofibers were obtained by high pressure homogenisation, then complexes of two Pickering stabilizers were prepared mixing the two dispersions. The main driving forces between them were hydrogen bonds and hydrophobic interaction, thus, regulating the interaction between these two components was proved as an effective method to modulate the physicochemical properties of emulsions.

Shi et al. (2016) fabricated novel film-forming emulsions based on zein-chitosan colloid particles fabricated by a simple antisolvent procedure; the Pickering emulsions were extremely stable, evidenced by the similar droplet sizes and size distribution in the film matrix. Interestingly, emulsion films exhibited excellent oxygen-barrier efficiency. This study opened a promising pathway for producing emulsion films with excellent oxygen-barrier capability via the manipulation of the film-forming emulsion's interfacial nanostructure using the Pickering stabilisation principle.

Dai et al. (2018) successfully prepared zein-gum arabic complex colloidal nanoparticles with a core-shell structure through hydrogen bonding and electrostatic interactions. The resulting emulsions were adequately obtained with high oil volume fractions (0.5–0.7). The complex nanoparticles absorbed efficiently at the O/W interface, forming steric barriers. Consequently, Pickering emulsion gels could be obtained with long-term storage stability and could become novel and effective delivery systems of bioactive compounds.

Another vegetal protein often used to form protein-polysaccharide complexes and conjugates is soy protein. X. Zhang et al. (2020) presented an easy method for making edible solid foams using Pickering emulsion technology. The O/W Pickering emulsions, stabilised by soy protein isolate and bacterial cellulose, exhibited smaller droplet sizes and better physical stability with increasing contents of complexes or with increased oil volume (Fig. 2). Further, the nanoscale soy protein isolate aggregates could adsorb on the bacterial cellulose nanofibril networks. Dynamic rheology results showed that all emulsions presented gel-like rheological behaviour, and both the shear viscosity and viscoelastic moduli increased with the increasing content of complexes or oil volume fractions.

Ashaolu and Zhao (2020) prepared a conjugate of soy protein isolate with okara dietary fibre by crosslinking using the Maillard reaction. The resulting soy protein isolate-okara dietary fibre conjugates were thermally stable, hydrophilic, and exhibited excellent Pickering emulsion stabilisation potential. In addition, the conjugates' structure and function relationships, amino acid profile, and emulsifying potential were favourable for formulating of emulsion-based foods.

A promising protein-polysaccharide complex was designed between gliadin and chitosan. Q. Li et al. (2019) studied Pickering emulsions stabilised by gliadin-chitosan nanoparticles (GCNPs). Three types of GCNPs structures, including primary complexation, soluble complexes, and coacervates were obtained by simply altering pH to produce different interaction levels. The reinforcement in gliadin-chitosan interactions reduced the surface charges of the particles and improved their wettability to absorb at the O/W interface. The gliadin-chitosan soluble complexes and coacervates stabilised more oil bridging droplets together, producing a strong network structure against coalescence. Moreover, the coacervate-stabilised Pickering emulsion had the highest viscoelasticity and solid-like behaviour. The findings showed such interactions can regulate either the stability, as the rheological, and antioxidant properties of GCNPs stabilised Pickering emulsion through changing the pH.

Khemissi et al. (2018) obtained protein microgels by heating whey protein isolate and mixed them with anionic or cationic polysaccharides; κ-carrageenan or chitosan, respectively. They found that small stable complexes can be formed with κ-carrageenan between pH 4.3 and 5.5 and with chitosan between pH 4.1 and 6.5, both below and above the isoelectric point of the microgels (pI = 5.0). The droplet size was found to be larger with κ-carrageenan than chitosan. Complexation of protein microgels with polysaccharides is a versatile method of modifying the properties of protein particles.

3.4. Pickering high internal-phase emulsions

Pickering stabilisers, which typically comprise solid or semi-solid particles, can be used to form stable HIPEs (Zamani, Malchione, Selig, & Abbaspourrad, 2018). HIPEs are highly concentrated gelled emulsions with an internal phase volume fraction (Φ) exceeding 0.74 (Cameron & Sherrington, 1996). An internal phase volume fraction exceeding this value results in the dispersed droplets reaching their maximum packing density, giving rise to highly viscoelastic flow behaviour. When the highest geometric limit for packing of rigid spheres is exceeded, the

liquid droplets in HIPEs are squeezed tightly together and typically develop polyhedral geometries. Texturally, HIPEs are highly viscous or gelled soft solid materials (Zamani et al., 2018). A high resistance to Ostwald ripening, coalescence, and phase separation is one of the advantages found in Pickering HIPEs over the conventional. This kind of HIPE has become a popular research topic due to their applicability in commercial products (Table 1) (Xiao, Li, et al., 2016).

Native proteins have been used as Pickering particles in HIPEs. Recently, Xu, Tang, Liu, and Liu (2018) reported that native ovalbumin of several nanometres is an outstanding Pickering stabiliser for O/W HIPEs, thanks to its strong intramolecular structural stability that ensures its particulate nature when adsorbed at an interface. These Pickering HIPEs exhibit an extraordinary stability against heating and long-term storage, unique responsiveness to freeze-thawing, and reduced volatile oil vaporization. In another recent study, Xu, Liu, and Tang (2019) demonstrated that native soy β-conglycinin (a major storage globulin in soybean), possessing similar structural features to ovalbumin, is another effective Pickering nanostabiliser for HIPEs.

Nevertheless, some native proteins need modifications to improve their emulsifying ability. Xu, Tang, and Binks (2020a) reported that bovine serum albumin glycated with galactose possessed a much stronger structural integrity and higher refolding ability. The authors showed improved HIPE emulsification and stabilisation when compared to native bovine serum albumin. A core-shell nanostructure formed with a hydrophilic galactose shell surrounding the protein core in glycated bovine serum albumin is the result of the underlying mechanism for improving emulsification performance. These HIPEs presented a self-supporting gel network that contributes to an enhanced stability under long-term storage, resistance to drastic heating and good freeze-thaw reversibility. In a similar way, Xu, Tang, & Bings (2020b) showed an ultra-efficient stabilisation of HIPEs using bovine serum albumin and trehalose as the model globular protein and polyol. A core-shell nanostructure with trehalose layer surrounding the bovine serum albumin is an interesting strategy that gave rise to a soft nanoparticle with a strong structural integrity and provided the formation of HIPEs with high extent of droplet bridging.

Yang, Li, and Tang (2020) obtained nanoparticles (160 nm) from some insoluble okara soy polysaccharides (a by-product of soybean processing) covalently attached to proteins in a glycoprotein matrix (arabinogalactan-proteins and glucomannan-proteins) that could perform as an outstanding Pickering stabiliser for HIPEs. The structure of the nanoparticles was stable, and the gels could be formed over their tested pH or ionic strength range. Moreover, these gels exhibited excellent stability during prolonged storage and heating up to temperatures between 50 and 90 °C. These nanoparticles exhibited an interesting potential to behave as Pickering stabilisers for emulsifying HIPES with ability to form HIPE gels. Moreover, using the high-added-value of the soybean by-product in their processing industries is advantageous.

Polysaccharides have also been used as Pickering particles in HIPEs. Zhu et al. (2020) successfully prepared stable O/W Pickering HIPEs stabilised by chitin nanofibrils. The high stabilisation ability of rod-like chitin nanofibrils originated from the restricted coarsening, droplet breakage, and coalescence upon emulsion formation. In addition to an irreversible adsorption at the interface it provided a fibrillar network highly interconnected in the continuous phase. Furthermore, the authors proposed a new manufacturing strategy for edible materials combining 3D printing and food-grade Pickering HIPEs. Their results demonstrated that chitin nanofibrils-stabilised HIPEs can fulfil the requirement of clean-labels for foodstuff and green materials.

Wang et al. (2018) showed that avocado oil based HIPEs were formulated and stabilised by citrus nanofibers (CNFs) and tannic acid (TA) by means of shear-induced emulsification method. CNFs/TA complex colloidal nanofibers with enhanced interfacial reactivity can be utilised for preparing stable avocado oil based HIPEs by one-step homogenisation. Forming an antioxidant interface using the interfacial cargo of TA further markedly enhanced the oxidative stability of the emulsions. This study offered valuable information to prepare polyphenol-nanofiber colloidal complexes and their use as antioxidants in food solutions.

Protein-polysaccharide particles formed with plant-based proteins are also remarkable for stabilising HIPEs. Zeng et al. (2017) reported the usage of mono-dispersed gliadin-chitosan hybrid particles as a particulate emulsifier for HIPEs development. The hybrid particles with partial wettability were fabricated at pH 5.0 using an easy antisolvent method. Stable HIPEs with up to an 83% internal phase can be prepared with low particle concentrations (0.5–2%). The hybrid particles were effectively adsorbed and anchored at the O/W interface to exert steric hindrance against coalescence. The protective effect of Pickering HIPEs on curcumin was confirmed and represents a sustainable alternative to convert polyunsaturated liquid oils into viscoelastic soft solids in replacement of hydrogenated oils.

Pickering HIPEs were prepared by Ma, Zou, McClements, and Liu (2020) by simply mixing an 15% v/v gliadin nanoparticle aqueous solution with gum arabic and corn oil (85% v/v). The gum arabic increased the apparent viscosity, storage modulus, and creaming stability of the HIPEs, resulting in an enhanced resistance to changes in pH, ionic strength, and temperature.

Hao, Peng, and Tang (2020) developed soy protein-based Pickering stabilisers for HIPEs to aid the emulsifying properties of proteins by glycation with carbohydrates. Soy glycinin, considered an important soy storage globulin, showed good performance as a Pickering stabiliser for HIPEs. In addition, its glycation with a soy soluble polysaccharide significantly improved the emulsification performance of the soy glycinin, the gel network formation, and stability against heating or freeze-thawing of the corresponding HIPEs. The HIPEs stabilised by untreated or glycated soy glycinin also presented great coalescence stability over long-term storage.

Protein-polysaccharide particles containing animal proteins, in this case dairy proteins, showed remarkable results as Pickering stabilisers. Zhu et al. (2020) investigated the application of whey protein isolate-low methoxyl pectin (WPI-LMP) particles, generated by complex coacervation, as a food-grade particle stabiliser. The coacervation pH greatly influenced the emulsifying ability of the WPI-LMP particles, which could generate an HIPE with an oil fraction up to 79%. However, the emulsification ability of the WPI-LMP coacervates was sensitive to ionic strength and their concentration. Bovine serum albumin is another interesting animal protein which forms a complex with polysaccharides. Liu, Zheng, Huang, Tang, and Ou (2018) have confirmed that modifying the surface of CNCs particles by bovine serum albumin absorption is an effective strategy to improve the emulsification performance. Authors reported the stiffness of HIPEs was attributed to a strong interaction and aggregation of bovine serum albumin-covered CNCs that enhanced droplet packing effect and formed 3D networks in the emulsion.

4. Conclusions

Food scientists and the food industry are in search of sustainable, cheap, clean-label, eco-friendly, and effective food-grade particles suitable to stabilise Pickering emulsions. Novel opportunities are emerging for the stabilisation of food emulsions using solid biopolymer nanoparticles and microparticles.

The primary advantage of solid biopolymer stabilisation is its longevity regarding coalescence, showing no significant structural changes, even as rather coarse droplets develop after several months. This is due to the effective steric structural barrier formed by the adsorbed solid particles. The stable biopolymer complexes formed by oppositely charged proteins and polysaccharides can produce and stabilise emulsions effectively. However, they can be influenced by many parameters including salt concentration, pH values, and the protein to polysaccharide ratio. In contrast, covalently crosslinked complexes are more permanent and stronger. Systems stabilised by these conjugates usually present great stability towards coalescence and, when the three-

dimensional network is formed in the continuous phase, creaming or sedimentation is impaired.

It is well-known that only a few solid particles are suitable for food industries. Good stabilisation of O/W emulsions has been reported when using prolamins in combination with other water-soluble polymers which, in turn, reduce the hydrophobicity of the prolamin particles. In addition, cellulose-based and chitin derivatives have attracted much attention due to their non-toxicity, biocompatibility, and biodegradability. Furthermore, chitosan and nanocelluloses satisfies the increasing demands for a sustainable and environmentally friendly stabiliser for Pickering emulsions.

Lastly, the interest in the development of gel-like emulsions has been growing due to the unique properties of three-dimensional solid-like behaviour that offer the emulsions a variety of applications in food industries. Pickering HIPEs formulated with the adequate solid particles have a promising potential to achieve long-term stable emulsions.

The current challenge entails translating the knowledge of emulsion stabilisation using solid particles into useful industrial applications. The presence of several possibilities boosts researches in order to select new suitable and clean-label ingredients that can improve existing formulations and explore new applications.

Declaration of competing interest

The authors declare no conflict of interests.

Author statement

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