Trends in Food Science & Technology 138 (2023) 671–684

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: www.elsevier.com/locate/tifs

Hybrid particles for stabilization of food-grade Pickering emulsions: Fabrication principles and interfacial properties

Nisufyan Nimaming, Amin Sadeghpour, Brent S. Murray, Anwesha Sarkar *

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

ARTICLE INFO

Handling Editor: Dr. S Charlebois

Keywords:
Mixed particles
Particle-stabilized emulsions
Oil-water emulsions
Polyphenols
Microgels
Release

ABSTRACT

Background: Colloidal particles have garnered considerable research attention in recent times for fabrication of Pickering emulsions (PEs) because of their distinctive ultra-stabilization properties in comparison to conventional emulsion stabilizers. Significant progress has been made in designing novel hybrid particles, *i.e.*, a combination of two or more materials comprising the particles, for tailoring emulsion stability as well as other functionalities that are not achievable with single particle-laden interfaces.

Scope and approach: We aim to provide a critical survey of the latest advances in food-grade hybrid particles that have been used to prepare Pickering emulsions in this review with an emphasis on the engineering of hybrid particles through various physical and chemical synthesis routes. In particular, we have examined the hybrid protein-polysaccharide, protein-phenolic compound, polysaccharide-lipid particles that have surfaced in the last five years with respect to their ability to stabilize and provide additional functionalities to PEs. We discuss recent studies on interfacial characterization of hybrid particles using interfacial (tension, rheology, Langmuir Blodgett), adsorption (quartz crystal microbalance with dissipation monitoring), microscopy and X-ray scattering techniques.

Key findings and conclusions: Synthesis of hybrid particles primarily depends on the properties of biopolymers: hybrid particles fabricated using water-insoluble biopolymers such as insoluble plant proteins exploit anti-solvent precipitation methods, whilst fabrication using water-soluble components usually involve covalent (alkaline treatment/oxidation/Maillard) or ionic interactions. Hybrid particles stabilize PEs *via* a combination of denser interfacial layer formation as well as bulk stabilization and offer benefits in protection/release of active lipidic ingredients versus single particle stabilizers.

1. Introduction

Emulsions are composed of two immiscible liquids with one liquid being dispersed (the dispersed or 'internal' phase) in another liquid (the continuous or 'external' phase). As well as being an integral part of many, if not most foods, emulsions are also extensively utilized for bioactive encapsulation, protection, and delivery of active pharmaceutical and nutraceutical compounds (Sarkar & Mackie, 2020). Generally, bioactive compounds are encapsulated within the dispersed phase by forming small droplets that range from 1 to 100 of μm in size, stabilized by emulsifiers or macromolecules. Emulsifiers such as surfactants or macromolecules play a crucial role in reducing the interfacial tension at the oil-water interface and tend to improve the kinetic stability of droplets and protect the encapsulated bioactive compounds against deterioration (Murray et al., 2021). However, such conventional emulsions are thermodynamically unstable leading to emulsion disruption *via* creaming/sedimentation, flocculation, coalescence, phase separation or Ostwald ripening, the rates of which are influenced mainly by the emulsifier properties. The utilization of alternative strategies for emulsion formation and long-term stabilization where solid particles are used to stabilize emulsion droplets, *i.e.*, Pickering emulsions (PEs) has attracted significant research focus among food scientists.

The outstanding stability of PEs is attributed to the almost irreversible attachment of solid particles at the oil-water interface, provided that they have the correct size and wetting properties. The detachment energy (ΔG_d (see equation (1)) to dislodge a particle can be extremely high – of the magnitude of several $1000k_BT$ (where, T is the absolute temperature and k_B is Boltzmann's constant) (Binks, 2002; Murray, 2019; Sarkar & Dickinson, 2020) *i.e.*, much higher that of conventional low molecular emulsifiers, where ΔG_d is almost always $<10\ k_BT$ per

* Corresponding author.
E-mail address: A.Sarkar@leeds.ac.uk (A. Sarkar).

https://doi.org/10.1016/j.tifs.2023.06.034
Received 14 March 2023; Received in revised form 10 June 2023; Accepted 30 June 2023
Available online 3 July 2023

molecule.

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

Here, r represents the radius of the Pickering particle, assumed spherical, γ_{ow} is the interfacial energy (tension) of the oil-water interface and θ is the equilibrium three-phase contact angle of the particle at the interface. The adsorption of solid particles and also deformable microgels at the interface occurs slowly and irreversibly by partially wetting both oil and water phases forming the particle-laden interfacial layer, resulting in a large steric barrier to droplet close approach and therefore ultrastability of the emulsions (Albert et al., 2019; Sarkar et al., 2019; Sarkar & Mackie, 2020). For instance, Du Le et al. (2020) demonstrated that by chemically modifying cellulose nanocrystals (CNCs) with hydrophobic groups wettability could be changed, with static contact angle altering from 56.0 ± 0.3° to 80.2 ± 0.8°, leading to formation of Pickering emulsions upon modification. Using nanofibers from various sources, an elegant study of Liu et al. (2023) suggested that modified cellulose nanofibers with an order of magnitude higher length could form stable Pickering emulsions with almost twice as high desorption energy (~3.41 × 10^3 k_BT) as compared to that by modified chitosan nanofibers (~320 nm), largely by virtue of their layer size. On the other hand, by deacylating chitin nanofibers and therefore changing the wettability (*i.e.* changing static contact angle from 35.69° to 84.38°) even with slightly smaller particle size (length ~254 nm), PEs could be fabricated with comparable detachment energy to that required for cellulose nanocrystals. Thus, besides the size of the particles, the wettability by either of the phases and henceforth the contact angle (see equation (1)) is also an important factor determining PE stabilization alongside particle shape, concentration, particle-particle interaction at the interface and environmental conditions (Destribats et al., 2014; Tavasoli et al., 2022).

The last decade has seen numerous publications confirming the utilization of solid particles for emulsion stabilization (Araiza-Calahorra & Sarkar, 2019; Dickinson, 2017; Marefati et al., 2017; Sarkar et al., 2016) to overcome some of the disadvantages of conventional emulsions. Besides their outstanding stability to coalescence, PEs are useful colloidal systems for protection and site-dependent delivery of bioactive ingredients due to their high encapsulation efficiency and resistance to disruption by intestinal bile salts. In addition, ingredient bioavailability under digestive conditions can be fine-tuned by altering the modulus, size, grafting and responsiveness of the particles to external stimuli (Araiza-Calahorra et al., 2020; Sarkar et al., 2016; Yang et al., 2020). There has been an increasing interest in the recent decade to design hybrid particles to overcome the weaknesses of single-component particles, either for achieving thicker interfacial layer or for offering controlled release and stimuli responsiveness to physiological stimuli.

Many studies have shown that modulation of particles by complexation with another species can improve their hydrophobicity and hence provide extra stability for PEs, particularly against various environmental and biochemical conditions where a single-moiety particle (*e.g.*, protein-based) might degrade (Chang et al., 2022; Dai, Zhan, et al., 2018; Sui et al., 2018; Tavasoli et al., 2022). Also, complexation of bioactive compounds to create PE-stabilizing particles is an interesting strategy for dual delivery of bioactive compounds. In other words, a bioactive compound can be delivered by being encapsulated in the dispersed phase whilst another (or the same) bioactive compound is delivered as the stabilizing hybrid particle at the interface, improving the loading and also the delivery.

In hybrid particles, often two or more biopolymers and/or particles are combined by physical or chemical means, including but not limited to: protein-polysaccharide hybrid particles (Dai, Zhan, et al., 2018; Jiang et al., 2021; Wijaya et al., 2020); combinations of proteins + phenolic compounds (Li et al., 2020; Su et al., 2020; Zhou, Yan, et al., 2018); complexation between particles and lipids (Atarian et al., 2019; Chen et al., 2021; Hosseini & Rajaei, 2020; Yan et al., 2022); particle-particle hybrids (Sarkar et al., 2018; Wei, Zhang, et al., 2021). Liu et al. (2018) studied the stabilization of high internal phase Pickering emulsions (HIPPEs) using cellulose nanocrystals (CNCs) or bovine serum albumin (BSA) on their own as well as their those stabilized by CNC + BSA hybrid particles. The results showed that neither BSA or CNCs alone was sufficient to provide long-term stability to the HIPPEs under certain environmental conditions. However, the HIPPEs stabilized by CNCs physically modified by BSA provided greater stability, where the combination of "sticky" CNC + BSA hybrid particles formed more closely packed networks at the interface. In another example, bioavailability of β-carotene was low when it was encapsulated in oil-in-water (O/W) PE droplets stabilized solely by wheat gluten nanoparticles (WGN) (Fu et al., 2019). However, β-carotene-loaded PEs stabilized by WGN-xanthan gum (WGN-XG) complexes were more stable and gave higher bioavailability. Addition of XG increased the thickness of particles at the interface, inhibiting chemical degradation of the β-carotene in the dispersed phase but somehow prevented droplet aggregation and thus, allowed better access of lipase molecules to droplet surfaces, increasing the quantity of β-carotene released into the micellar phase (Fu et al., 2019). In another example, the release of free fatty acids was decreased using gliadin (GLD)-proanthocyanin (PACN) complexes (GCHPs) compared to the PEs that were solely stabilized by GLD particles (Zhou, Yan, et al., 2018). It is hypothesized that such robust hybrid particles structure at the interface reduced the accessibility of the lipase to the oil phase during digestion and limited the rate of lipolysis. The hybrid particles formed by antioxidants potentially eliminated free radicals, avoiding proximity between pro-oxidants and primary oxidant products, and restricted the diffusion of pro-oxidants toward the interfaces. In view of this increasing functionality, besides offering stability, food-grade hybrid particles are attracting considerable attention in literature to stabilize PEs.

To date most published reviews have focused on particles prepared with solely proteins or polysaccharides. In the latter, modifications either by physical or chemical methods are employed to enhance particle hydrophobicity (Ribeiro et al., 2021). There has been some mention of hybrid particles (Ashfaq et al., 2022; Chang et al., 2022; Ribeiro et al., 2021; Tavasoli et al., 2022) but to our knowledge there is no review that focuses on the principles of fabrication and more importantly the interfacial film properties of the hybrid particles at the droplet surface. This literature review thus aims to provide an advanced understanding of the fabrication of edible hybrid particles stabilizing PEs, focusing on mechanisms of interaction between the components of the hybrid particles and their interfacial properties, that have surfaced in the last five years. It is important to highlight that hybrid particles here refer to particles that have been fabricated using more than one component and that where mixtures of one or more particles have been employed to stabilize PEs. Terminologies such as "composite", "complex" or "mixed" particles have been used in literature, and therefore are included in this review. We cover protein-polysaccharide, protein-phenolic and polysaccharide-lipid hybrids, plus dual/multiple particle systems. We identify their benefits versus non-hybrid counterparts, particularly in view of stabilization when subjected to different environmental conditions or active encapsulation. Key attention has been given to discuss the range of interfacial and nanostructural techniques that have been employed to characterize the morphological and interfacial properties of these hybrid particles. Finally, we provide future perspectives on PEs stabilized by hybrid particles and opportunities that remain unexplored. The abbreviations used in this review can be seen in Supplementary Table S1.

2. Hybrid particle formation

Different food-grade materials have been used for hybrid particle formation based on the use of polar solvents, covalent and non-covalent interactions. Different preparation routes such as the Maillard reaction, solvent-anti-solvent exchange, complexation using pH and ions and

grafting with various functional groups have been used, resulting in various kinds of hybrid particle morphology in the nm to μm size range, as shown in Fig. 1.

We have classified these hybrid particles into protein-polysaccharide, protein-phenolic, polysaccharide-lipid and particle-particle hybrids and compared their stabilization properties with their non-hybrid analogues (see Tables 1–4 for physicochemical characteristics) in the following sections. We have covered specific examples in these sections, discussed their microstructure (Fig. 2) showing the ranges of size of PEs obtained using hybrid particles and also included some functionalities such as enacpsulation of lipidic compunds.

2.1. Hybrid protein-polysaccharide particles

Proteins and polysaccharides are the two most commonly used biopolymers for designing hybrid Pickering stabilizers. Such particles have been developed using covalent bonding *i.e.* condensation between amino groups of the proteins and free aldehyde/ketone groups of the polysaccharides, whilst electrostatic interactions, ionic bonds, hydrophobic as well as van der Waals attractive forces and hydrogen bonding are examples of non-covalent interactions that have also been exploited in their fabrication (Ashfaq et al., 2022; Ribeiro et al., 2021; Tavasoli et al., 2022). Some recent examples of hybrid protein-polysaccharide particles and their corresponding PEs are summarized in Table 1. Often the choice of preparation method depends on the initial solubility of the protein in the polar solvent (usually water). If the protein is completely insoluble or has limited solubiliity in the aqueous medium, solvent precipitation is generally the preferred fabrication route, whereas if the protein is soluble, electrostatic complexation is utilized.

Plant storage proteins that are rich in prolamin, such as zein (ZN) and gliadin (GLD), often have an aggregated structure with limited solubility, dispersibility and poor wettability in aqueous media which prevents their use as classic Pickering stabilizers in their own right (Sarkar & Dickinson, 2020). Therefore, hybrid particle formation using another biopolymer has been found to be beneficial. Zein found in maize, has poor dispersibility in both oil and aqueous phases and cannot stabilize O/W or water-in-oil (W/O) emulsions efficiently (Dai et al., 2018a, 2018b). It is noteworthy that ZN contains significant proportions of non-polar amino acids with distinct hydrophobic regions that can be exploited to drive the formation of aggregates *via* the antisolvent precipitation route (Dai et al., 2018a, 2018b; Ma et al., 2021; Shah et al., 2021). Complexation between ZN and polysaccharides has been investigated in order to overcome ZN's poor dispersibility in any polar solvent and weakness as a sole particle stabilizer (Table 1). For instance, Dai, Zhan, et al. (2018) employed 70% (v/v) ethanol-water solutions of ZN for the preparation of ZN-propylene glycol alginate (PGA) nanoparticles (ZPGAPs) *via* antisolvent precipitation. The addition of PGA interrupted the formation of large ZN-ZN aggregates (1400 nm) and thus the particle size of the hybrid ZPGAPs was significantly smaller (around 350 nm at a ZN: PGA ratio of 10 : 1, w/w), they had a spherical shape but with rough surfaces (Fig. 1A).

The three-phase contact angle ($\theta_{o/w}$) of ZPGAPs was greater upon this hybridization over sole ZN aggregates, making the former more suitable for O/W emulsion stabilization via better wettability by either of the two phases. Additionally, the ZPGAP-stabilized PEs (droplet size of ~20 μm - see Table 1) were more stable to coalescence, with a dense coverage by ZPGAPs (Dai, Zhan, et al., 2018). Likewise, Sun et al. (2017) synthesized ZPGAPs at pH 4.0 using antisolvent precipitation and found that the particle size decreased with an increase of PGA concentration. The ZPGAP morphology was rough and branch-like and ZPGAPs-stabilized PEs exhibited high encapsulation efficiency, allowing for functional ingredient delivery systems (Sun et al., 2017). Dai, Sun,

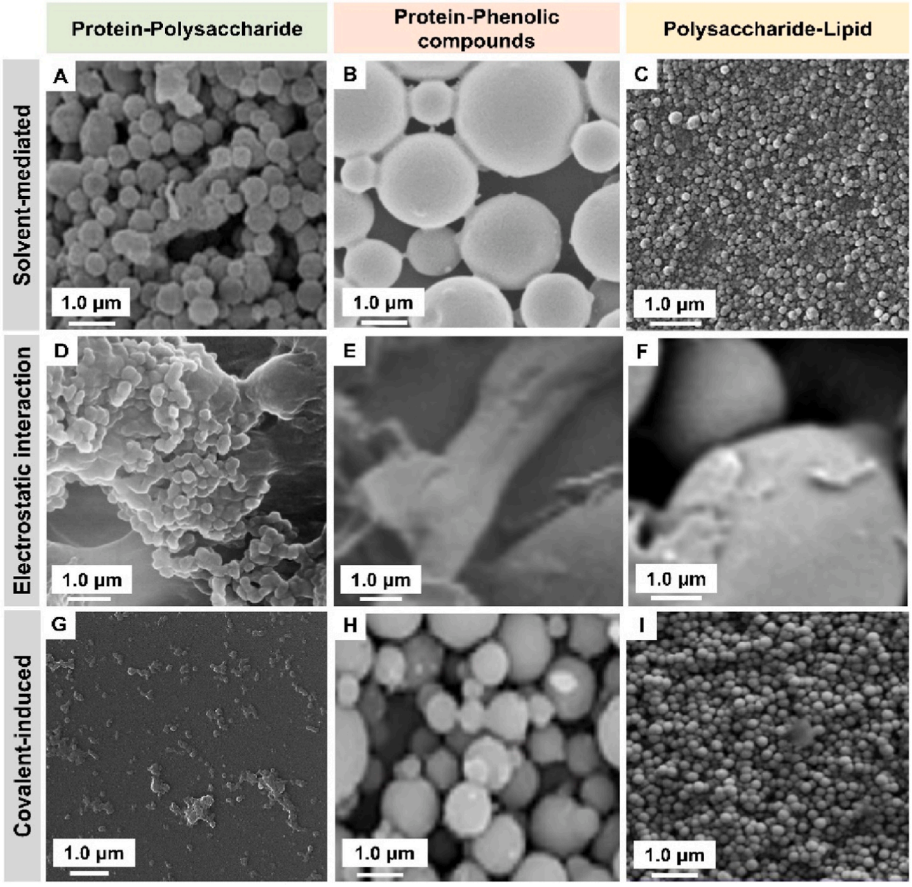

Fig. 1. Scanning electron micrographs (SEMs) of edible hybrid particles for Pickering emulsion stabilization prepared by solvent-mediation: (**A**) zein (ZN)- propylene glycol alginate (PGA) (Dai, Zhan, et al., 2018), (**B**) ZN-epigallocatechin-3-gallate (ZN-EGCG) (Liu et al., 2017), (**C**) high-amylose corn starch (HACS)-palmitic acid (PA) (Yan et al., 2020); electrostatic interaction: (**D**) soy protein isolate (SPI)-chitosan (CS) (Yang et al., 2020), (**E**) SPI-curcumin (CUR) (Du et al., 2022), (**F**) HACS-lauric acid (LA) (Chen et al., 2021); and covalent-induced routes, respectively: (**G**) whey protein microgel (WPM)-maltodextrin (Sengupta et al.) (pH 8.0) (Karbasi & Askari, 2021), (**H**) ZN-CA (Xu et al., 2022), (**I**) CS-SA nanogels (Atarian et al., 2019), respectively. Micrographs are used with permission from Elsevier (images **A-E**, **G-I**), and American Chemical Society (image **F**). Images **A**, **E**, **F** and **H** have been scaled to allow the same scale bar usage for all images.

Table 1
Fabrication methods and physicochemical properties of hybrid protein-polysaccharide particles for making Pickering emulsions.

Hybrid protein-polysaccharide particles	Preparation method	Particle characteristics			Emulsion characteristics		References
		Ratio (w:w)/Conditions (pH/ions/solvent/temperature)	Particle size (nm)[a]	Particle shape	Compositions[b]	Droplet size (μm)[c]	
Water soluble protein-polysaccharide particles							
Pea protein isolate (PPI)-High methoxyl pectin (HMP)	Electrostatic interaction	PPI: HMP (1:1)/Degree of methylation of pectin (DM): 72%/pH 2.0–7.0	379	spherical	80.0 wt% corn oil (CO) 1.0 wt% PPI-HMP	38	Jiang et al. (2021)
WPI-Dextran (DX)	Covalent bonding	WPI: DX (1:2)/pH 7.0–11.0$WPDX_{10}M$ (microgel with 11% degree of conjugation)	125	spherical	20.0 wt% Medium-Chain Triglyceride oil (MCT oil) 1.0 wt% $WPDX_{10}M$	10	Araiza-Calahorra et al. (2020)
Water insoluble protein-polysaccharide particles							
Zein (ZN)-gum arabic (GA)	Solvent-mediated	ZN: GA (5:1 to 1:5) (ZGAPs)/pH 4.0/70% aqueous ethanol	~225	Irregular shape	10.0–70.0 w/v% MCT oil 1.0 w/v% ZGAPs	17[d]	Dai, Sun, et al. (2018)
ZN-Propylene glycol alginate (PGA)		ZN: PGA (40:1 to 1:1) (ZPGAPs)/pH 4.0/70% aqueous ethanol	346	spherical	30.0–75.0 v/v% 0.2–2.0 w/v% ZPGAPs	20[d]	Dai, Zhan, et al. (2018)
Water soluble protein-water insoluble polysaccharide particles							
SPI-Bacterial cellulose nanofibers (BCNFs)	Electrostatic interaction	SPI: BCNFs (3:1 to 9:1)/pH 3.0	–	fibrous network	20.0 wt% MCT oil 1.0 wt% SPI-BCNFs	~20	Zhang, Wu, et al. (2022)
SPI-chitosan (CS)		SPI: CS (40:1)/pH 5.2–5.4/acetic acid	149	spherical	50.0–65.0 wt% CO 1.5–3.5 wt% SPI-CS	12	Yang et al. (2020)
PPI-CS		PPI: CS (1:4 to 4:1)/pH 7.0/acetic acid	194	irregular and round with rough surface	40.0–60.0 wt% CO 0.5–4.0 wt% PPI-CS	34	Ji et al. (2022)
Water insoluble protein-water insoluble polysaccharide particles							
ZN-CS	Solvent-mediated	ZN: CS (20:1)/70% aqueous ethanol-acetic acid (ZCPs)	~100	spherical	50.0 wt% CO 2.0 wt% ZCPs	30–40	Ma et al. (2021)
Gliadin (GLD)-CS		GLD: CS (20:1)/pH 3.0–7.0/75% aqueous ethanol-acetic acid (GCNPs)	180[d]	–	50.0 wt% CO 2.1 wt% GCNPs	18	Li, He, et al. (2019)

[a] hydrodynamic diameter (D_h) of the lowest sized particle reported irrespective of the conditions of preparation.
[b] composition of the particle reported is the total biopolymer concentration used to make the particle used in the emulsion.
[c] droplet mean size corresponds to the $D_{4,3}$ values (only of the lowest sized droplet reported irrespective of the conditions of preparation).
[d] particle/droplet sizes were estimated from graphs.

et al. (2018) created core-shell structured zein-gum arabic particles (ZGAPs), where ZN and gum arabic (GA) were postulated to interact *via* both electrostatic interactions as well as hydroden bonding. Although the particle size of ZGAPs was larger than the non-hybrid ZN-based nanoparticles, the contact angle of the hybrid ZGAPs was closer to 90 °, which gave the ZGAPs a better wetting property and generated a steric barrier against oil droplet aggregation. Besides stabilization, hybrid particles often provide additional functionlaity. Using ZN-based hybrid particles, Liang et al. (2021) demonstrated that the release of tannic acid (TA) encapsulated in pectin-ZN hybrid particles (PZDs) was slow during the first 120 min of digestion compared to unencapsulated TA, which is fully released after 60 min. However, the TA showed rapid release in the first 30 min in the small intestine phase in which ZN was hydrolyzed by trypsin. This meant PZDs were effective for preservation of bioactive compounds under the stomach phase and allowed for delivery at targeted intestinal sites unlike the non-hybrid ZN-based particle-stabilized PEs.

Gliadin (GLD) is another prolamine-rich protein, abundant in wheat, sorghum and other cereals, containing a higher proportion of hydrophobic amino acid residues that can also be used to produce particles *via* solvent-mediated methods. Wang et al. (2021) illustrated the formation of GLD-sodium alginate (ALG) coacervate particles (GSCPs), held together by electrostatic interactions at pH 3.5. The GSCPs prevented droplet coalescence and Ostwald ripening (Wang et al., 2021) of corresponding O/W PEs. In another system, GLD-chitosan (CS) nanoparticles (GCNPs) were prepared by Li, He, et al. (2019) at different pH values (3.0–7.0). The smallest particle size was 180 nm and was obtained at the lowest pH attributed largely to electrostatic interaction between charged groups of GLD and CS, which gave PE a mean droplet size of around 18 μm (Table 1). This study showed that not only the thick interfacial surface layer formed by these hybrid particles at the droplet surface contributed to the stability but also network formation between GLD and CS bridging droplets in the bulk phase (Sarkar & Dickinson, 2020). This highlights the importance of hybrid particles acting as "glues" where the two components offer many sites of bonding between particles attached to the same or neighboring droplets as compared to single Pickering stabilizer, thus offering not only interfacial but also bulk phase networking inducing additional stability (Zembyla et al., 2019).

Moving to rather insoluble and widely abundant natural polysaccharides such as cellulose, formation of hybrid particles has also shown intriguing properties as PE stabilizer when cellulose is mixed with proteins, to improve their wettability. Cellulose is not biodegradable by human gastrointestinal enzymes (Sarkar et al., 2019), and thus can be an excellent candidate for controlled release mechanisms. However, even if some domains are hydrophobic, cellulose in general is often not wettable by oil on its own due to its overall hydrophilic nature. Zhang, Wu, et al. (2022) prepared PEs stabilized by complexing bacterial cellulose nanofibrils (BCNFs) with soy protein isolate (SPI). SPI nanoparticles complexed with BCNFs *via* electrostatic attraction at pH lower than 4.5 showed a fibrous structure due to interlinked microfibrils of BNCF covering the SPI nanoparticles. These complexes stabilized PEs with a mean droplet of 20 μm (Table 1) and exhibited a synergistic inhibition of FFA release during *in vitro* digestion. It was proposed that the compacted hybrid particulate layers at the interface restricted transport of bile salts and lipases to the oil droplet surface, and hence resulted in delayed lipid digestion (Zhang, Wu, et al., 2022). Thus, formation of

Table 2
Fabrication methods and physicochemical properties of hybrid protein-phenolic particles for making Pickering emulsions.

Hybrid protein-phenolic compound particles	Preparation method	Particle characteristics			Emulsion characteristics		References
		Ratio (w:w)/Conditions (pH/ions/solvent/temperature)	Particle size (nm)[a]	Particle shape	Compositions[b]	Droplet size (μm)[c]	
Protein-soluble phenolic compounds							
ZN-Tannic acid (TA)	Solvent-mediated	ZN: TA (1:0.5)/pH 3.0 and 5.0/ethanol (ZTPs)	68	spherical	50.0 wt% Sunflower oil (SFO) 2.0 w/v% ZTPs	9[d]	Zou et al. (2019)
GLD-Proanthocyanidins (PAC)		GLD: PAC (1:1 to 10:1)/pH 4.0/70% ethanol-water-acetic acid (GPHPs)	87	spherical	50.0 wt% CO 0.5 wt% GPHPs	53	Zhou, Yan, et al. (2018)
Pea protein (PP)-PAC	Electrostatic interaction	PP: PAC (3:1 to 1:1)/pH 7.0	150	–	3.0 wt% flaxseed oil (FSO) 0.6 wt% PP-PAC	~200[f]	Dai et al. (2020)
PP-TA		PP: TA (1:0.1 to 1:0.5)/pH 7.0	–	–	5.0 wt% FSO 1.0 wt% PP-TA	<1[d]	Li et al. (2020)
Ovalbumin (OVA)-TA		OVA: TA (2:1)/pH 3.0–6.0	–	–	80.0 wt% Dodecane, 1 wt% OVA-TA	11[e]	Chen et al. (2022)
SPI-anthocyanin (ACN)	Covalent bonding	SPI: ACN (6:0.05 to 6:0.15)/pH 7.0, 300 mM NaCl, 95 °C/15 min	186	spherical	20.0 v/v% SBO 4.8 wt% SPI-ACN complex	15–20	Ju et al. (2020)
Protein-insoluble phenolic particles							
SPI-CUR		SPI: CUR (2: 10 to 2: 70 w/μM), SPI-Cur-NPs/ethanol	118	flake-like	10.0–40.0 wt% MCT oil 2.0 wt% SPI-Cur-NPs	3–5	Du et al. (2022)

[a] hydrodynamic diameter (D_h) only of the lowest sized particle reported irrespective of the conditions of preparation.
[b] composition of the particle reported is the total biopolymer concentration used to make the particle used in the emulsion.
[c] droplet mean size corresponds to the $D_{4,3}$ values (only of the lowest sized droplet reported irrespective of the conditions of preparation).
[d] droplet mean size corresponds to the $D_{3,2}$ values (only of the lowest sized droplet reported irrespective of the conditions of preparation).
[e] particle/droplet sizes were estimated from graphs.
[f] droplet mean size is measured in nm.

Table 3
Fabrication methods and physicochemical properties of hybrid polysaccharide-lipid particles for making Pickering emuslions.

Hybrid polysachharide-lipid particles	Particle characteristics			Emulsion characteristics		References
	Concentration (wt%)/Conditions (pH/ions/solvent/temperature)	Particle size (nm)[a]	Particle shape	Compositions[b]	Droplet size (μm)[c]	
Enzymatically hydrolyzed starch (EHS)- Palmitic acid (PA)	5.0 wt% EHS 5.0 wt% PA/pullulanase for enzymatic hydrolysis of starch/ethanol	500	spherical	10.0 wt% CO 0.5 wt% EHS-PA	357	Yan et al. (2022)
High amylose corn starch (HACS)-Lauric acid (LA)	3.0 wt% HACS 0.6 wt% LA/~70% amyose in HACS/ethanol	1315[e]	spherical	30.0 wt% CO 4.0–6.0 wt% HACS-LA	10	Chen et al. (2021)
CS-stearic acid (SA) nanogels	1.0 wt% CS 0.5 wt% SA/ethanol-aceic acid	–	spherical	20.0 wt% sunflower oil (SFO) 1.0 wt% CS-SA nanogels	20[d]	Atarian et al. (2019)
	1.0 wt% CS 0.5 wt% SA//ethanol-aceic acid	100	spherical	20.0–60.0 wt% fish oil (FO) 1.0–2.0 wt% CS-SA nanogels containing CEO	~25[d]	Hosseini and Rajaei (2020)

[a] hydrodynamic diameter (D_h) only of the lowest sized particle reported irrespective of the conditions of preparation.
[b] composition of the particle reported is the total biopolymer concentration used to make the particle used in the emulsion.
[c] droplet mean size corresponds to the $D_{4,3}$ values (only of the lowest sized droplet reported irrespective of the conditions of preparation).
[d] particle/droplet sizes were estimated from graphs/micrographs.
[e] particle size of the Pickering stabilizer corresponds to the $D_{4,3}$ values (only of the lowest sized droplet reported irrespective of the conditions of preparation).

hybrid particles can open new opportunities for using various biopolymers which otherwise offer limited capability as PE stabilizers.

Shifting the focus to proteins that have better dispersibility in aqueous media than the aforementioned prolamine-rich particles, the preparation of hybrid particles of protein + polysaccharides often occur *via* electrostatic and ionic interactions. For example, electrostatic interactions between oppositely charged proteins and polysaccharides using pectin or chitosan is a common route for fabricating hybrid particles (Falsafi et al., 2022; Tavasoli et al., 2022) with improved performance. For instance, Ji et al. (2022) synthesized pea protein isolate (PPI)-CS nanoparticles (Table 1). The PPI-CS nanoparticles stabilized PEs containing eicosapentaenoic acid (EPA) and had a mean droplet size of 34 μm but more importantly resulted in the delayed release of EPA during *in vitro* digestion, which was attibuted to the gel-like structure of these hybrid nanoparticles (Fig. 2c). Yang et al. (2020) complexed CS to SPI to generate spherical SPI-CS nanoparticles with a mean size of 149 nm. Here the particles formed a connected structure rather than individual particles (Fig. 1D). SPI-CS-stabilized PEs showed complete particle coverage, stability to thermal treatments and a range of ionic conditions, which therefore offered excellent capacity for bioactive compound encapsulation and protection (Yang et al., 2020) as compared to PEs prepared using just SPI nanoparticles. In another study, Jiang et al. (2021) have designed hybrid particles of high methoxyl pectin (HMP) and PPI formed by electrostatic complexation. The PPI-HMP particles were spherical with the smallest size ≈379 nm, which was greater than the pure PPI particles. However, the HIPPESs stabilized by the PPI-HMP particles (Fig. 2a) allowed better retention of β-carotene loaded into the droplets at pH 6.0 after 30 days due to the larger

Table 4
Fabrication methods and physicochemical properties of hybrid particle-particle systems.

Hybrid particle-particle systems	Preparation method	Particle characteristics			Emulsion characteristics		References
		Ratio (w:w)/ Conditions (pH)	Particle size (nm)[a]	Particle shape	Compositions[b]	Droplet size (μm)[c]	
Inulin nanoparticle (INP)-Lactoferin nanogel particles (LFN)	Electrostatic interaction	INP: LFN (3:1)/pH 7.0	116 (INP) 101 (LFN)	both are spherical	20.0 wt% SFO 3.0 wt% INP + 1.0 wt% LFN	9	Sarkar et al. (2018)
Plant protein microgel (PPM)-CNCs		PPM: CNCs (1:1 to 1:3)/pH 3.0	250 (PPM) 100 (CNCs)[d]	spherical with needle-shaped	20.0 wt% sunflower oil 1.0 wt% PPM + CNC (1.0–3.0 wt%)	14	Zhang et al. (2021)
ZN-PGA (ZPCPs)-Whey protein microgel (WPM)		ZPCPs: CNCs (4:1 to 1:4)/pH 4.0	454 (ZPCPs) 56 (WPM)	both are spherical	50.0 wt% MCT oil containing 3.0 wt% BC 1.5 wt% WPM + 1.5 wt% ZPCPs	27	Wei, Zhang, et al. (2021)

[a] hydrodynamic diameter (D_h) only of the lowest sized particle reported irrespective of the conditions of preparation.
[b] composition of the particle reported is the total biopolymer concentration used to make the particle used in the emulsion.
[c] droplet mean size corresponds to the $D_{4,3}$ values (only of the lowest sized droplet reported irrespective of the conditions of preparation).
[d] particle/droplet sizes were estimated from micrographs – the size of CNC represents the longest dimension.

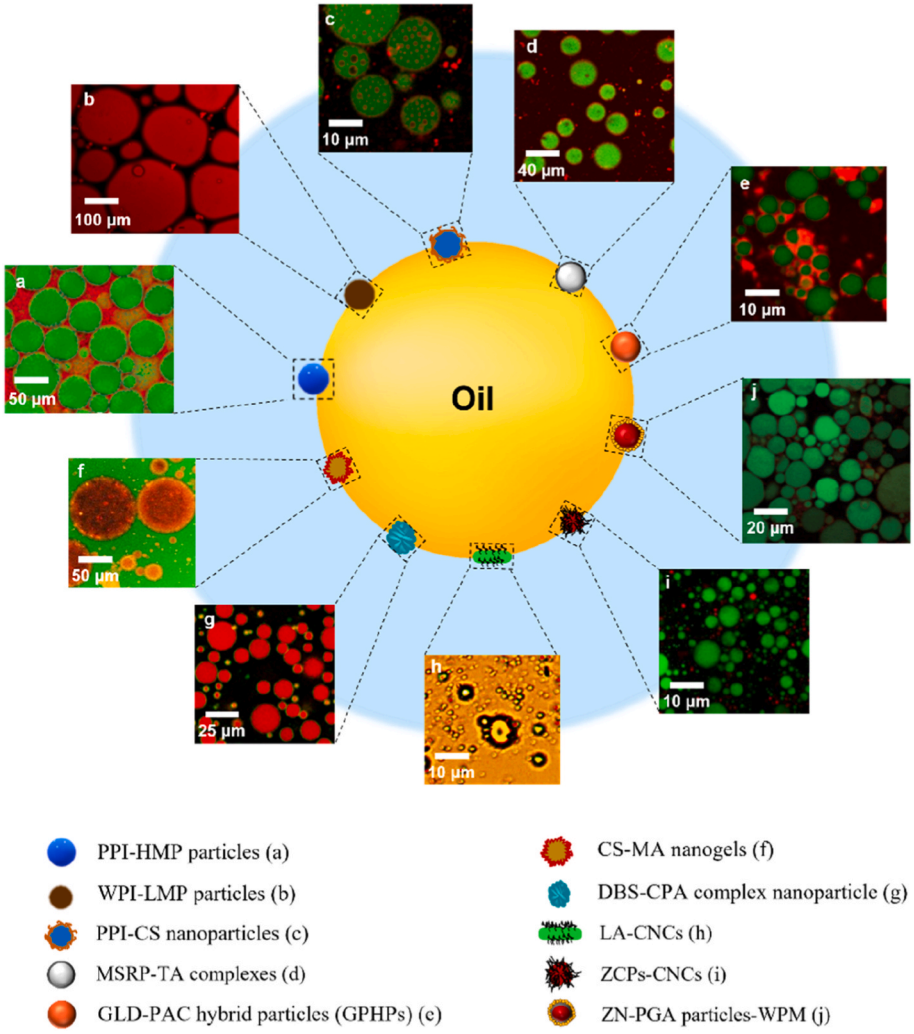

Fig. 2. Diagrammatic illustration of O/W Pickering emulsions stabilized by food-grade hybrid particles. The image presents confocal micrographs of oil droplets stabilized by (**a**) pea protein isolate (PPI)-high methoxyl pectin (HMP) colloidal particles (Jiang et al., 2021), **(b)** whey protein isolate (WPI)-low methoxyl pectin (LMP) particles (Zhu et al., 2021), **(c)** pea protein isolate (PPI)-chitosan (CS) nanoparticles (Ji et al., 2022), **(d)** moringa seed residue protein (MSRP)-tannic acid (TA) complexes (Huang et al., 2022), **(e)** gliadin (GLD)-proanthocyanidins (PAC) hybrid particles (Zhou, Yan, et al., 2018), **(f)** chitosan (CS)-myristic acid (MA) nanogels (Hosseini et al., 2020), **(g)** debranched starch (DBS)-capric acid (CA) complex nanoparticle (Jia et al., 2022), **(h)** lauric acid (LA) adsorbed-cellulose nanocrystals (CNCs) (Patel et al., 2022), **(i)** zein colloidal particles (ZCPs)-Cellulose nanocrystals (CNCs) (Wei, Liu, et al., 2021), **(j)** zein (ZN)-propylene glycol alginate (PGA) particles-whey protein microgels (WPM) (Wei, Zhang, et al., 2021). Micrographs are used with permission from Elsevier (images **a, c, d, g, h**), Taylor & Francis Group (image **b**), American Chemical Society (image **e, i**), Spinger Link (image **f**), and Royal Society of Chemistry (image **j**).

thickness of the PPI-HMP particles surrounding the oil droplets as compared to single PPI particles (Table 1).

Besides electrostatic interactions, the Maillard reaction has also been investigated extensively for protein and polysaccharide conjugation to enhance the functional characteristics of proteins in general and improve their steric stabilization of droplets. However, using this reaction to create hybrid particles is a relatively recent endeavor (Araiza-Calahorra et al., 2020). The Maillard reaction involves conjugation between an amino group - usually the terminal amino group of a protein - and the reducing monosaccharide end of the polysaccharide (Ashfaq et al., 2022). Generally, the protein-polysaccharide ratio, polysaccharide molecular weight, temperature, relative humidity (RH),

reaction time, and pH value are major factors affecting the conjugation. To validate covalent bonding between the protein and polysaccharide, the non-conjugated free amino groups are detected by *ortho*-phthalaldehyde (OPA) method and expressed as the degree of conjugation (DC) (Araiza-Calahorra et al., 2020). Araiza-Calahorra et al. (2020) used pH and conjugation reaction time to manipulate the degree of conjugation (DC) of whey protein isolate (WPI) with dextran (DX) to create hybrid WPI-DX microgel particles. The results revealed that higher pH values and conjugation time promoted WPI-DX conjugation. The WPI-DX microgel particles obtained were spherical and 125 nm in diameter (Table 1). These WPI-DX microgels showed great efficiency in delaying *in vitro* digestion of PEs (Araiza-Calahorra et al., 2020) which was a significant advantage over just WPI-based microgels. Zhang, Yue, et al. (2022) found that a mass ratio of SPI: DX of 1:1.75 and incubation for 3.3 days were optimum for SPI-DX conjugation - the DC obtained was 26.97%. The corresponding SPI-DX nanogels had particle diameters ≈100 nm with a core-shell structure. PEs stabilized by these hybrid nanogels showed enhanced stability to thermal treatment and NaCl addition (0–200 mM) compared to PEs stabilized by their SPI counterparts. These studies again highlight the advantages of hybrid protein-polysaccharide particles over their non-hybrid counterparts offering better stability under environmental and biological conditions.

2.2. Hybrid protein-phenolic particles

Phenolic compounds are found in many fruits and vegetables and possess strong antioxidant activities, possibly helping to prevent certain chronic diseases. Their chemical structure is composed of at least one phenolic moiety but frequently this is conjugated to several other cyclic carbon rings bearing other hydroxyls with or without conjugated sugars (Czubinski & Dwiecki, 2017; Liu et al., 2021). Hybrid particle formation between proteins and phenolic compounds thus has the potential to create emulsifying entitities that also have enhanced antioxidant capacity by having antioxidant bearing species in the Pickering stabilizer itself (Li et al., 2021; Quan et al., 2019). Hybrid protein-phenolic compound particles can be constructed by either non-covalent or covalent interactions (Table 2), with the latter providing higher physicochemical performance such as, stability to environmental variations (*e.g.* pH, ionic strength) (Ashfaq et al., 2022; Liu et al., 2021; Pham et al., 2019; Quan et al., 2019).

A range of phenolic compounds with varying degree of dispersibility in aqueous phases has been used to create hybrid particles. Tannic acid (TA) complexes with proteins have been investigated several times in literature with a view to improving the properties of PEs. TA can be solubilized in concentrated ethanol–water solutions and thus it is possible to co-dissolve it with insoluble ZN and use antisolvent precipitation to create ZN-TA hybrids. Zhou et al. (2020) prepared ZN-TA complex particles (ZTPs) with different mass ratios. These hybrid ZTPs particles had lower sizes (60 nm) as compared to sole ZN particles (100 nm). At a mass ratio of ZN: TA of 1:1, the ZTPs were spherical and smooth. More importantly, PEs stabilized by ZTPs demonstrated a greater long-term stability against droplet coarsening, creaming and oxidation as compared to those stabilized by ZN particles alone - see Table 2.

Another class of phenolic compounds - proanthocyanidins (PAC) have shown high affinity for proteins. Zhou, Yan, et al. (2018) demonstrated that pure GLD tends to self-assemble, which was limited in the presence of PAC. The particle size of GLD-PAC particles (GPHP) increased at 2% PAC before decreasing at 10% PAC (0.5% GLD final content). PEs stabilized by these hybrid GPHP had a mean droplet size of 53 μm (Fig. 2e) as well as enhanced stability to coalescence, which was believed to due to the formation of a network-like hybrid particule structure covering the droplet surfaces. The PEs also showed reduced free fatty acid release during simulated gastrointestinal digestion. Dai et al. (2020) demonstrated that the addition of grape seed proanthocyanidins (GPAC) to PPI at pH 7.0 resulted in PP-GPAC complexes with a relatively high negative charge with their size being significantly reduced (150 nm) as compared to PPI. More importantly, such PEs stabilized by hybrid PP-GPAC particles had good coalescence stability to pH, heating, ionic strength as compared to single PPI particles (Dai et al., 2020) (Table 2).

The ease of complex formation during fabrication of hybrid particles varies greatly depending on exactly which protein and polyphenol are combined and under what conditions, particularly the pH. Liu et al. (2017) demonstrated that the complexation of ZN with either epigallocatechin-3-gallate (EGCG), quercetagetin (QT) or chlorogenic acid (CA) can enhance the functionality of ZN to act as a PE stabilizer. In comparison to non-covalent bonding, the conjugation of ZN with the aforementioned phenolic compounds had a high grafting efficiency under alkaline treatment (pH 9.0) because the polyphenols were oxidized and covalently reacted with the sulfhydryl or amino acid side chains of proteins. The ZN-EGCG complex particles, possessing a smooth surface and spherical shape (see Fig. 1B), produced PEs with the highest stability to thermal treatment and highest antioxidant activity compared to all the other hybrid particles studied (Liu et al., 2017).

Hydrogen bonding and hydrophobic interactions are the two main non-covalent forces dominating the hybrid particle fabrication *via* proteins and phenolic compounds, whilst ionic interactions have a relatively minor role (Quan et al., 2019). For instance, Chen et al. (2022) investigated the addition of TA to ovalbumin (OVA) under different pH values. In comparison to single OVA particles, OVA-TA complexes had significantly enhanced particle wettability at pH lower than 6.0, with θ closer to 90°, which gave smaller (<15 μm) droplets and increased the stability of the corresponding HIPPEs (Table 2). A dense network structure of hybrid particles formed at the oil droplet surface and particles formed at lower pH were shown to be more highly (negatively) charged (Chen et al., 2022). Additional functionality could be achieved by hybrid particle formation. For instance, Li et al. (2020) showed that fabricating hybrid PPI-TA complexes offered with better resistance to oxidation (Table 2) as compared to single PPI particle-stabilized systems.

Curcumin (CUR) is a water-insoluble polyphenol found in turmeric (*Curcuma longa*) that is thought to have health benefits. Crystals of CUR have been shown to act as a Pickering stabilizer (Zembyla et al., 2018) but with limited stability and capability to encapsulate large propertions of water. SPI-CUR nanoparticles of size 118 nm Du et al. (2022) prepared *via* hydrophobic interactions were flaky (see Fig. 1E) and had higher three-phase contact angle ($\theta_{o/w}$) of 80.6° as compared to CUR alone. These particles could stabilize emulsion droplets in the size range of 3–5 μm (Table 2) and the droplets displayed a densely packed network (gel-like) structure, highlighting again the significance of bulk stabilization as well as just interfacial stabilization *via* hybrid particles, largely attributed to the inter-droplet hydrophobic interactions by CUR within the SPI-CUR nanoparticles. Lipid oxidation of the PEs appeared to be effectively reduced by the CUR associating with the SPI at the interface again illustrating the beneficial effects of hybrid particle formation.

A range of chemical and biochemical processing routes such as alkaline conditions, enzymatic reactions and free radical grafting have been utilized to create hybrid protein-phenolic particles *via* covalent bond formation. Alkaline reactions are usually carried out at pH 9.0, leading to the oxidation of the phenolic groups. Ju et al. (2020) demonstrated that increasing the anthocyanin (ACN) concentration under alkaline treatment enhanced the conjugation of SPI to ACN. The SPI-ACN hybrid particles were smaller and more hydrophobic compared to single SPI nanoparticles, in agreement with Sui et al. (2018). PEs stabilized by SPI-ACN particles had mean droplet sizes between 15 and 20 μm and their surfaces showed a porous honeycomb-like structure of particles, as well as much higher stability to autoxidation. Xu et al. (2019) demonstrated that infact the contents of free amino acid, thiol and tyrosine groups were lowered on free radical grafting of WPI to chlorogenic acid (CA), suggesting that these groups were involved in the reaction with CA within the hybrid particles. Similar results have been

found by Xu et al. (2022) for ZN conjugated to CA or gallic acid (GA), prepared *via* the carbodiimide-mediated coupling method. The conjugation altered the ZN particles, making them smooth and spherical (see Fig. 1H). The surface hydrophobicity of these hybrid ZN-CA and ZN-GA particles was considerably higher than pure ZN particles, resulting in improved wettability and consequently stability of the corresponding PEs as well as better stability to heating and autoxidation.

2.3. Hybrid polysaccharide-lipid particles

Polysaccharides contain a large number of hydroxyl groups and therefore tend to be hydrophilic in nature. Hence, often they are functionalized with lipids to create particles to improve their wettability by the hydrophobic oil phase. Particularly, starch and chitosan have been extensively combined with lipids (Table 3) to create polysaccharide-lipid complex particles. The formation of starch-lipid complexes is usually performed *via* thermal treatment and the binding mechanism is most often *via* hydrogen bonding or ionic interactions (Sengupta et al., 2022). Lu and Huang (2019) prepared high-amylose corn starch (HACS)-fatty acid complexes using oleic (OA), stearic (SA), palmitic (PA), myristic (MA) or lauric (LA) acids *via* hydrothermal treatment. As one might expect, the HACS-fatty acid complexes had significantly greater hydrophobicity than the untreated starch granules. The main location of fatty acid binding was thought to be to the amylose helices. PEs stabilized by the HACS-fatty acid particles were more stable to coalescence, thermal treatment and lipolysis, depending on the fatty acid carbon chain length (Lu & Huang, 2019).

Yan et al. (2020) investigated HACS complexed with *n*-caproic acid (NCA) (Wei et al.), LA or PA and confirmed that the longer carbon chain length fatty acids gave greater degree of complexation due to increased hydrophobic interaction with the hydrophobic helix interior of amylose. The HACS-PA nanoparticles were spherical and approximately 250 nm in size (see Fig. 1C). Yan et al. (2022) also demonstrated that limited enzymatic hydrolysis of HACS contributed to PA being complexed to HACS in the hybrid particles (see Table 3) and were excellent stabilizers of PEs. In fact Chen et al. (2021) illustrated that on forming hybrid HACS-LA complexes (Fig. 1F), the θ increased from 44.5 to 79 ^{o} and resulted in more monodisperse PEs of mean droplet size $\approx$ 10 μm (Table 3).

Chitosan (CS) is among the very few positively charged naturally occurring biopolymers at neutral pH and has been used to create 'nanogels' as PE stabilizers (Shah et al., 2016; Yan et al., 2017). However, CS-based non-hybrid nanogels are relatively hydrophilic and therefore complexation with fatty acids improves their PE stabilizing performance by improving their wettability by the hydrophobic oil phase. For instance, Kuroiwa et al. (2021) demonstrated that complexation between CS and OA was largely *via* electrostatic and hydrophobic interactions. PEs stabilized by CS-OA complexes ranging in size from 300 to 1000 nm successfully encapsulated CUR (Kuroiwa et al., 2021). Hosseini and Rajaei (2020) have also demonstrated the successful incorporation of clove essential oil (CEO) into CS-stearic acid (SA) hybrid particles (Table 3). Formation of thick interfacial layers of CS-SA nanogels coating the fish oil droplets, plus the incorporated CEO enabled extended the chemical stability to up to 14 days. Besides encapsulation of bioactives, Atarian et al. (2019) demonstrated that spherical CS-SA nanogels (Fig. 1I) prepared using the 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC)-mediated reaction (Croisier & Jérôme, 2013) provides stability to wide pH variations and lipid autoxidation, unachievable with solely CS-based nanogels.

2.4. Hybrid particle-particle systems

Recently, particle-particle systems have surfaced in literature, which have been used to stabilize PEs and provide interesting functionalities, such as controlled lipid digestion of the encapuslated lipids. By hybrid particle-particle systems we mean cases where more than type of particle associates at the interface – examples are summarized in Table 4. In other words, particles can be added sequentially or in a mixed system but at the point of addition they are mixture of two or more particles rather than one particle of multiple chemical components. The interactions between such two or more colloidal particles at the interface can be electrostatic, hydrophobic or hydrogen bonding (Sarkar et al., 2018; Wei, Guo, et al., 2021).

Sarkar et al. (2018) fabricated lactoferrin nanogels (LFNs) of size 100 nm by heat-induced disulfide crosslinking. The LFNs were highly positively charge at neutral pH, whilst inulin nanoparticles (INPs) of size 115 nm, derived *via* enzymatic hydrolysis, had a slight negative charge. PEs stabilized by LFNs were first formed, then INPs added, forming an additonal layer *via* elecrostatic attraction between the oppositely charged particles (see Table 4). The PEs with hybrid particles not only had a greater stability to coalescence but also showed slower *in vitro* gastric digestion, believed to be due to the more closely packed mulilayers of INPs and LFNs at the O–W interface as compared to PEs coated solely by LFNs (Sarkar et al., 2018). Zhang et al. (2021) also prepared pea protein microgels (PPM) of size 250 nm by heat-induced treatment at pH 7.0. The PPM were positively charged at pH 3.0. When negatively charged CNCs were added, synergistic particle-particle complexes were formed at the interface that delayed *in vitro* gastric pepsinolysis and consequently gastric-induced coalescence of emulsions.

Hybrid ZN-PGA particles (ZPCP) have also been shown to interact with oppositely charged WPMs at the oil-water interface in a similar manner (Wei, Zhang, et al., 2021) to those LFN-INP mentioned previously (Sarkar et al., 2018) (Table 4). The ZPCPs, size 454 nm, were prepared by antisolvent precipitation and whilst WPMs were prepared by heat-induced gelation (56 nm). Both types of particle were spherical and combination of these two individual particles allowed stabilizing PEs of mean size of 10 μm (Fig. 2j) that showed resilience to coarsening when subjected to a wide range of ionic strengths and pH conditions. When the PEs stabilized by ZPCPs + WPM were loaded with β-carotene, the bioaccessibility of β-carotene was enhanced, particularly when the WPMs formed the outer layer of ZPCP-stabilized PEs (at WPM: ZPCPs ratio of 1:4). This was believed to be due to the adsorption of the smaller WPMs into the gaps between the larger ZPCPs at the interface. This system also restricted lipase access to the droplets and enhanced the stability, breakdown and absorption of β-carotene in the *in vitro* gastrointestinal regimes (Wei, Zhang, et al., 2021).

In summary, there have been two clear motivations for creating hybrid particles to develop PEs (Tables 1–4).

a. *Biological applications.* For delivering antioxidant species such as phenolic compounds, both dispersed and at the interface, researchers have attempted to create phenolic compound-based particles to stabilize PEs. However, such polyphenolic compounds need hybridization with proteins to provide wetting properties appropriate for adsorption at oil-water interfaces. On the other hand, to make starch much more resistant to amylases, there has been motivation to covalently bind starch with lipids, which in turn gives hydrophilic starch some hydrophobic character to wet both oil and water phases. The work done on developing hybrid particles with phenolic compounds has largely used physical approaches, whereas hybrid particles using lipids via chemical treatment might not have clean-label status for food applications.
b. *Functional applications.* There is a clear interest in using plant protein-based particles to design sustainable food-grade PEs. Often plant proteins have high surface hydrophobicity (Dai, Sun, et al., 2018; Ji et al., 2022) and adding polysaccharide groups to them enhances hydrophilicity and better wetting at oil-water interfaces. This is the reason why most work on hybrid particles is done with plant proteins, with limited work on dairy proteins.

Irrespective of their type, hybrid particles stabilize PEs by a combinations of interfacial as well as bulk stabilization mechanisms. The

presence of one or more additional components essentially improves wettability, thus enhancing preferential adsorption at the droplet surface and coalescence stability of the PEs. Moreover, often that additional component offers new binding sites allowing hybrid particles anchored to different droplets to form a network in the bulk phase, adding to the bulk stabilization of the droplets. Hybrid particles (Tables 1–4) offer a range of additional functional benefits such as better stability to variations in environmental and processing conditions such as ionic strengths, pH and temperatures, plus greater resistance to chemical (autoxidation) or enzymatic (pepsin and lipase) degradation during gastrointestinal digestion.

Nevertheless, in attempting to understand the key interfacial role of

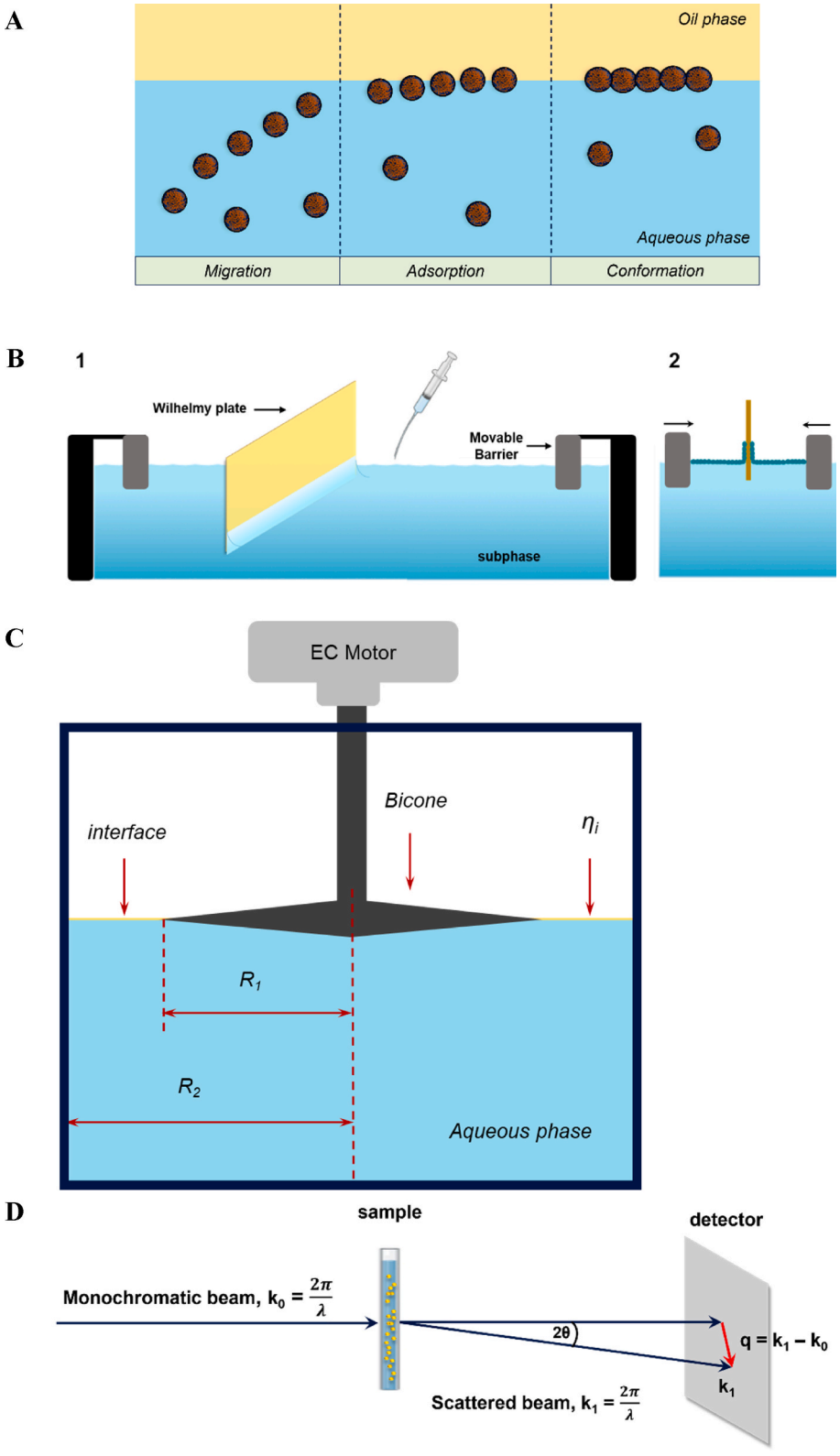

Fig. 3. Schematic illustration of the stages in the formation of an adsorbed particle layers (**A**), and interfacial techniques for hybrid particles. Langmuir trough (**B**) with spreading of colloidal hybrid particles on the subphase (water phase) (**B1**), Langmuir-Blodgett (LB) is created using a Langmuir trough with a substrate (**B2**). An interfacial bicone-based shear rheometry (**C**) to measure interfacial shear viscosity (η_i) of the hybrid particles at the oil-water interface. R_1 and R_2 are the radius of rotational disk and the cylindrical container, respectively. The basic SAXS experimental setup for structural investigation of hybrid particles (**D**).

hybrid particles, very few studies have characterized hybrid particles in details at the oil-water interface. We cover such studies and discuss a few of the most relevant interfacial and structural techniques that might be used in the future to evaluate the beneficial role of hybrid versus non-hybrid particles.

3. Interfacial properties of hybrid particles and techniques

It is evident that where hybrid particles are superior to their non-hybrid counterparts in terms of increased PE stability, some advantages in terms of the factors controlling the detachment energy ΔG_d (equation (1)) or the kinetics of adsorption must be conferred *via* the formation of the hybrid particle. This might be due to a change in surface hydrophobicity (and hence θ), particle size or advantageous structuring of the particulate layers at the interface. Often the hybrid particles are designed empirically without in-depth interfacial characterization of the hybrid particles versus the non-hybrid components. In this section, we review a selected suite of techniques that have been used to investigate these changes in hybrid particles, or that could be applied in the future to clearly understand if formation of hybrid particles offers any benefit to interfacial properties of PEs. Mass transport of particles to the interface in PE formation is *via* a combination of diffusion and convection (Fig. 3A), the latter of which can be extremely intense when emulsions are formed in high shear mixers and homogenizers. Not surprisingly, most methods of directly monitoring formation of an adsorbed particle film are restricted to low convection scenarios, where diffusion is thought to dominate.

QCM-D. The quartz crystal microbalance with dissipation monitoring (QCM-D) is an ultrasensitive method that has emerged as one of the most practical techniques for measuring the properties of adsorbed biopolymers and particles at solid piezoelectric surfaces. Adsorption at different sensor surfaces in real-time is relatively easy to monitor (Dixon, 2008) and can be a rapid screening tool for predicting what combination of materials and what ratios might give the best stabilizers. The approach is based on the evolution in resonance frequency of a quartz crystal when a particle dispersion attaches to a solid surface, which is used to further compute the mass of particles adsorbed (Fauzi et al., 2021; Wijaya et al., 2020). The quartz surface can be pre-coated with a variety of materials to make it mimic a hydrophobic-aqueous (*e.g.*, O–W) interface with varying degrees of success (Xu et al., 2020; Zembyla et al., 2021).

Wijaya et al. (2020) used QCM-D to investigate the adsorption behavior of hybrid WPI-low methoxyl pectin (LMP) particles with different ratios of LMP at pH 4.5. The quartz substrate used was a hydrophilic gold sensor, which was coated with 1-hexadecanethiol to create a hydrophobic surface to simulate oil surface. As WPI-LMP particles were introduced and came in contact with the hydrophobically modified sensors, the negative frequency shift (Δf) demonstrating that the hybrid WPI-LMP particles adsorbed on the sensor surface whilst a rapid increment of the dissipation (ΔD) highlighted the viscoelastic nature of the hybrid particle layers. By observing the change in thickness and mass adsorption onto the hydrophobic sensor it was evident that the addition of LMP to WPI in different ratios enhanced the viscoelasticity of the adsorbed layers of hybrid particles at the interface (Wijaya et al., 2020).

Zhang, Wu, et al. (2022) investigated the adsorption BCNF-SPI complexes *via* QCM-D at pH 3.0 on a quartz crystal sensor coated with MCT oil. Compared to the adsorption of solely SPI or BCNF, the hybrid BCNF-SPI particles formed rather rigid and thin layers. A limited proportion of BCNFs actually contributed to the adsorbed layer and the BCNF/SPI ratio could be optimized in the hybrid BCNF-SPI particles to allow formation of more compact interfacial layers. A mass ratio of BCNF: SPI of 1:5 showed the greatest surface adsorption. Thus, QCM-D can be a powerful technique to screen the best ratio of components to design hybrid particles that give the optimum thickness or viscoelasticity. Such interfacial techniques are now starting to capture research attention in the hybrid particle formation community.

Interfacial tension. Reduction of the interfacial tension (γ) is fundamentally associated with occupation of interfacial sites by surface active species, reducing the interfacial contact area between the two immiscible liquid phases. Any technique that measures γ can therefore be employed to monitor the kinetics of adsorption, though pendant drop and Wilhelmy plate tensiometers are most widely used. However, for classic, perfectly solid Pickering particles, there is virtually no lowering of the macroscopic γ until the close-packed, space-filling network of particles is formed, in which case the macroscopic interface is effectively 'removed'. For the case of hybrid Pickering stabilizers composed of various biopolymers, lipids *etc.* the situation is more complex. Firstly, there may be some surface-active sections of polymer chains within or at the surface of these hybrid particles that can still access and adsorb to the interface in the same way as free biopolymeric surfactant. In addition, surface active components may be released to some extent at the interface, plus there are likely to be at least some free surface-active species present that were not completely incorporated into the particles in the first place. Furthermore, such particles are unlikely to be completely solid but viscoelastic, as noted above, so that they may deform at the interface in order to reach a state of lowest free energy, which may also be connected with some of the complicating factors mentioned above. For these reasons, measurements where γ is simply monitored over time may not be so revealing, whereas measurements where the interface is deliberately compressed or expanded at different times and the γ response is measured, may tell us more about the nature of the adsorbed film.

Qin et al. (2021) measured γ verus time for various concentrations of hybrid WPI-EGCG conjugated nanoparticles *via* the pendant drop method compared with WPI. For the conjugate nanoparticles, γ was lower than for WPI, indicating higher hydrophobicity of the conjugates. Su et al. (2020) reported significantly different surface activity of β-lactoglobulin (β-lg) versus hybrid particles such as β-lg-EGCG complexes, β-lgNPs, and β-lgENPs (the mass ratio of β-lg: EGCG at 15: 1). For β-lg and β-lg-EGCG, γ declined considerably in the first 150 s before reaching an equilibrium value, whereas β-lgNP and β-lgENPs showed only a slight decrease in γ over the first 150 s that then remained constant over time (Su et al., 2020). Likewise, Su et al. (2021) also reported that 1.0 wt% β-lgNPs showed a rapid initial reduction in γ (first 300 s), while β-lg and its hybrid conjugated particles fabricated with PGA (1.0 wt% β-lgPNPs) showed only a slight decrease in γ over this same time, before reaching a constant value of γ that was not as low as that of β-lgNP. In fact, PGA molecules promoted structural changes in the hybrid β-lgNP + PGA-coated surfaces. The coating of PGA molecules to the β-lgPNPs might have contributed to a large number of hydroxyl groups at the surface of the hybrid particles resulting in the modest reduction in γ. In other words, this suggest that not all hybrid particles may reduce γ and careful fabrication of particles is important when thinking about using hybrid particles for stabilization of PEs.

Monolayer experiments. The response of an adsorbed layer of colloidal particles to expansion and compression is one of the crucial elements determining how they stabilize colloidal systems (Bergfreund et al., 2021). In a Langmuir trough, the interface is contained within movable barriers so that the interfacial area can be altered whilst γ is monitored. Particles can be allowed to adsorb to the interface from the bulk phase, or, if they are sufficiently and strongly adsorbing, they can be spread at the interface, in which case a particle monolayer is formed of known particle surface density, *i.e.* known (mean) are per particle (Fig. 3B). The particle monolayers can then be compressed or expanded to investigate particle structuring and interactions within the monolayer, plus their response to any changing subphase conditions. Furthermore, the interfacial structures can be carefully transferred to a solid substrate *via* the classic Langmuir-Blodgett methodology, which then allows investigation of the particle structures by *via* other techniques, such as various types of microscopy (Binks, 2002; Li, Lilja, et al., 2019). These techniques lend themselves well to monolayers at the

air-water (A-W) interface. Application to O–W interfaces is more difficult and less common, but is possible. The γ – trough area relation is most usually expressed in the form of interfacial pressure (π) – area (A) isotherms, where π is simply the reduction in γ of the clean interface (*i.e.*, devoid of particles) and A is the mean area per particle.

Very limited monolayer experiments have been performed using food-grade hybrid particles. Zhou, Huang, et al. (2018) studied monolayers of hybrid zein-high methoxyl pectin particles (ZPHPs) spread on an aqueous subphase of deionized water at pH 3.8. The monolayers were then transferred to a Langmuir-Blodgett film on mica, dried and sputter-coated with gold, then examined *via* scanning electron microscopy. At higher mass ratio of pectin to ZN, the network architecture of spherical particles became more noticeable. This was explained by the pectin coating the ZN, increasing the electrostatic and steric barriers and decreasing the hydrophobic attraction between the particles, preventing them from aggregating at the surface into dense clumps but forming more open, chain-like networks.

Zhang et al. (2021) investigated the π-A isotherms of the hybrid particle-particle system of PPM and CNC at the A-W interface. At acidic conditions (pH 3.0), the isotherms for spreading PPM (positively--charged) and CNC (negatively-charged) together were considerably different than when spreading PPM alone, due to electrostatic attraction between CNC and PPM and henceforth complex hybrid layer formation at the interface. However, when CNC was added to PPM already spread, there was no change in the isotherm, suggesting that the CNC merely formed secondary particle-particle layers on top of the PPM when added after PPM adsorption. Spread monolayers of CNC alone could not be formed, presumably due to the high (negative) charge on the CNCs, making them too hydrophilic. These proposed interactions were reflected in the corresponding stability of PEs stabilized by these different systems. More studies are needed using Langmuir-Blodgett film methodology to study the film formation mechanism and mechanical response of hybrid particles versus non-hybrid particles.

Interfacial rheology. Interfacial rheology has also been used to explore the adsorbed particle behavior at liquid-liquid or air-liquid phases (Murray, 2002). The interface can be subjected to a deformation or speed of deformation and the corresponding interfacial stress monitored, or *vice versa*. However, two tpyes of deformation must be distinguished – dilatational and shear deformation. Dilatational refers to a change in area, whereas shear refers to a change in shape (but not area). The importance of the distinction lies in the fact that dilatational deformations result in a change in the surface density of the inerfacial particles, whereas for shear deformation the mean surface density is constant, although the shear may result in changes in local structure and density througout the particle layer. In interfacial dialtational rheology the corresponding stress is the $\Delta\gamma$ ($\Delta\pi$), whereas for interfacial shear rheology the shear stress is monitored *via* disks (Fig. 3C), rings or tracer particles positioned at the interface. Interfacial dialtational rheology measurements are thus easily performed *via* Langmuir trough or pendant drop methods where the trough or drop area can be readily varied and the corresponding γ monitored. By analogy with bulk rheology, for viscoelastic layers of bioploymer-based particles and the like, one can distinguish elastic (storage) and viscous (loss) components of both dilatitional and shear interfcial rheology (Erni et al., 2003; Murai et al., 2015). Numerous measurements have shown that η_i is extremely senstive to the strength of the interactions between the film components, which of course in the context of this review depends upon the nature and composition of the components within the hybrid particles at the interface, as well as any factors such as pH, ionic strength, temperaure, *etc.*, that alter this strength and the mciroscopic structure of the adsorbed film of particles (Araiza-Calahorra et al., 2020; Murray, 2002; Murray & Dickinson, 1996; Zembyla et al., 2018).

Araiza-Calahorra et al. (2020) used such a biconical disk system to study η_i of hybrid whey protein-dextran conjugated microgel particles (WPDxM), formed by Maillard cross-linking, at pH 7.0 at the *n*-tetradecane-water interface. The values of η_i for both WPDxM and WPI nanogels (WPN) (at 0.5 wt% particles) increased rapidly to very high values in the first 3 h before, followed by a slow decrease over the next 24 h, although η_i for WPDxM remained much lower than that of corresponding WPI-based nanogel particles. This was explained by high attractive interactions between the WPI-based nanogel particles at the interface, as for β-lg molecules themselves when they unfold at an interface via the multiplicity of the same types of internal bonds determining protein structure. The hybrid WPDxM particles adsorbed and interacted less with their neighboring particles due to the steric repulsion introduced by the dextran chains attached to the protein. Again, there is limited literature on the interfacial rheology of hybrid particles but this is important in order to understand the nature of the film formed and compare them with non-hybrid analogues really pin point the benefit of fabricating hybrid particles.

X-ray scattering. Investigation of the structure of individual hybrid particles is crucial for elucidating their characteristics in PE systems. For the structural studies, small angle scattering is an effective method for the investigation of biological macromolecules in terms of internal core-shell structures, conformational changes or the arrangement of biomolecules without requiring their fixation, or vitrification procedures. The contrast variations in the samples are the source of the scattering signals, which determine the intensity and shapes of molecules (Fan & Wang, 2019). Small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) can be used to investigate the colloidal structural characteristics of particles including hybrid particles.

Generally, SAXS determines X-ray scattering at angles less than 10° which offers information about the wide range of molecular size, shape, and arrangement of particles and complexes in the system (Fan & Wang, 2019; Larson-Smith et al., 2012). In SAXS, X-rays interact with atomic electrons, and the number of electrons determines the X-ray scattering length density (Fig. 3D). For neutron scattering, neutrons interact and scatter elastically with atomic nuclei, and scattering patterns disclose the structure and spatial arrangement of the material (Da Vela & Svergun, 2020; Fan & Wang, 2019).

Use of scattering to decipher the structure of hybrid particles is relatively uncommon in literature. Kuroiwa et al. (2021) utilized SAXS to investigate the structural properties of hybrid CS-OA particles. The results demonstrated peak scattering pattern, $q = 1.5\ nm^{-1}$ for CS-OA complex, but the solutions of both CS and OA did not show this peak. The characteristic spacing (d) of the CS-OA complex structure was 4.2 nm, indicating the aggregated structure of OA molecules forming lamellar-like structures resembling bilayers (Kuroiwa et al., 2021). In another study, Guo et al. (2021) used SAXS to investigate the microstructure of rice starch-unsaturated fatty acid complexes with different concentrations, using *trans*-2-dodecaenoic acid (t12), *trans*-oleic acid (t18), *cis*-oleic acid (18) and linoleic acid (loa) treated by high-pressure homogenization (HPH). The SAXS patterns revealed that the lamellar structure of rice starch was disrupted by the HPH treatment, resulting in the disappearance of the rice starch structure. As the concentration of unsaturated fatty acids was increased from 1 to 3% in the hybrid particles, the fractal dimension increased demonstrating that the complex structure was more ordered and compacted. SAXS also demonstrated that as the length of the unsaturated fatty acid chain increased, the microstructure of the rice starch-unsaturated fatty acids complex became more organized.

Apart from conformational change evaluation, there are plenty of applications of SAXS studies are plenty in terms of particle adsorption and interaction at the interface, such as oleic acid adsorbed silica particles (Sadeghpour et al., 2013), the vertical position (contact angle), inter-particle distance of core-shell nanoparticles at liquid-liquid interfaces (Isa et al., 2013) as well as understanding the size, structure and aggregation of starch nanoparticle (Apostolidis et al., 2023). To sum up, although laboratory-synthesized hybrid particles are now populating the literature space in fabricating PEs as well as encapsulation of bioactives, detailed characterization of hybrid particles using sophisticated structural and interfacial techniques is still limited and needs more

attention in the future.

4. Conclusions and future perspectives

Colloidal particles as stabilizers have gained significant research attention owing to their ultra-stabilization mechanism of Pickering emulsions and hybrid particles do offer unique stabilization benefits over single particles, particularly under environmental conditions. Hybrid particle formation can be performed with proteins, polysaccharides, phenolic compunds and/or lipids, mainly through solvent mediation, covalent and non-covalent interactions based on the functional properties of biopolymers, particles and conditions, respectively. Plant proteins in particular have been the choice for making hybrid particles because plant proteins are often difficult to wet by water or oil phases and need an additional component to allow effective wetting and adsorption at the oil-water interface. In addition, extensive studies have been performed on the fabrication of hybrid particles to stabilize PEs for encapsulating and releasing bioactive components. In particular, phenolic compounds have been the choice in this regard due to the phenolic compounds' functionality in terms of antioxidant activity. Hybrid particles in general exhibit superior functionality particularly in terms of wettability, adsorption behavior and consequently long-term stability. However, often such stabilization is a result of interfacial properties as well as bulk stabilization conferred by the hybrid particles. Despite a significant number of studies on the development of hybrid particles for PE stabilization, thorough examination of structure and interfacial properties of hybrid particle remain untackled, which is necessary for tailoring effective hybid particle design. Such knowledge of structure-function relationships could enable optimization for both stabilization and controlled release.

Since phenolic compounds are often used to engineer food-grade hybrid particles, future studies should also look at focusing on understanding dual delivery of bioactives both in the dispersed phase and at the interface as a potential application of hybrid particle-stabilized emulsion. Last but not the least, future studies should look at sensory properties and the biodegradation processes of these hybrid particles and the corresponding PEs in the gastrointestinal tract, using both *in vitro* and *in vivo* studies, before such hybrid particles can be fully exploited in real food and beverage applications.

Data availability

No data was used for the research described in the article.

Acknowledgements

Author NN acknowledges financial support from Rajamangala University of Technology Krungthep (RMUTK), Thailand, for a PhD academic scholarship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tifs.2023.06.034.

References

Albert, C., Beladjine, M., Tsapis, N., Fattal, E., Agnely, F., & Huang, N. (2019). Pickering emulsions: Preparation processes, key parameters governing their properties and potential for pharmaceutical applications. *Journal of Controlled Release, 309*, 302–332. https://doi.org/10.1016/j.jconrel.2019.07.003

Apostolidis, E., Stergiou, A., Kioupis, D., Sadeghpour, A., Paximada, P., Kakali, G., & Mandala, I. (2023). Production of nanoparticles from resistant starch via a simple three-step physical treatment. *Food Hydrocolloids, 137*, Article 108412. https://doi.org/10.1016/j.foodhyd.2022.108412

Araiza-Calahorra, A., Glover, Z. J., Akhtar, M., & Sarkar, A. (2020). Conjugate microgel-stabilized Pickering emulsions: Role in delaying gastric digestion. *Food Hydrocolloids, 105*, Article 105794. https://doi.org/10.1016/j.foodhyd.2020.105794

Araiza-Calahorra, A., & Sarkar, A. (2019). Pickering emulsion stabilized by protein nanogel particles for delivery of curcumin: Effects of pH and ionic strength on curcumin retention. *Food Structure, 21*, Article 100113. https://doi.org/10.1016/j.foostr.2019.100113

Ashfaq, A., Jahan, K., Islam, R. U., & Younis, K. (2022). Protein-based functional colloids and their potential applications in food: A review. *Lebensmittel-Wissenschaft & Technologie, 154*, Article 112667. https://doi.org/10.1016/j.lwt.2021.112667

Atarian, M., Rajaei, A., Tabatabaei, M., Mohsenifar, A., & Bodaghi, H. (2019). Formulation of Pickering sunflower oil-in-water emulsion stabilized by chitosan-stearic acid nanogel and studying its oxidative stability. *Carbohydrate Polymers, 210*, 47–55. https://doi.org/10.1016/j.carbpol.2019.01.008

Bergfreund, J., Bertsch, P., & Fischer, P. (2021). Effect of the hydrophobic phase on interfacial phenomena of surfactants, proteins, and particles at fluid interfaces. *Current Opinion in Colloid & Interface Science, 56*, Article 101509. https://doi.org/10.1016/j.cocis.2021.101509

Binks, B. P. (2002). Particles as surfactants—similarities and differences. *Current Opinion in Colloid & Interface Science, 7*(1), 21–41. https://doi.org/10.1016/S1359-0294(02)00008-0

Chang, C., Li, J., Su, Y., Gu, L., Yang, Y., & Zhai, J. (2022). Protein particle-based vehicles for encapsulation and delivery of nutrients: Fabrication, digestion, and release properties. *Food Hydrocolloids, 123*. https://doi.org/10.1016/j.foodhyd.2021.106963

Chen, Y., Liu, Y., Liu, H., & Gao, Y. (2021). Preparation of lauric acid modified high-amylose cornstarch by a solvothermal process and its pickering emulsion. *ACS Food Science & Technology, 1*(5), 845–853. https://doi.org/10.1021/acsfoodscitech.1c00058

Chen, Y., Yi, X., Zhang, Z., Ding, B., Li, Z., & Luo, Y. (2022). High internal phase Pickering emulsions stabilized by tannic acid-ovalbumin complexes: Interfacial property and stability. *Food Hydrocolloids, 125*, Article 107332. https://doi.org/10.1016/j.foodhyd.2021.107332

Croisier, F., & Jérôme, C. (2013). Chitosan-based biomaterials for tissue engineering. *European Polymer Journal, 49*(4), 780–792. https://doi.org/10.1016/j.eurpolymj.2012.12.009

Czubinski, J., & Dwiecki, K. (2017). A review of methods used for investigation of protein–phenolic compound interactions. *International Journal of Food Science and Technology, 52*(3), 573–585. https://doi.org/10.1111/ijfs.13339

Da Vela, S., & Svergun, D. I. (2020). Methods, development and applications of small-angle X-ray scattering to characterize biological macromolecules in solution. *Current Research in Structural Biology, 2*, 164–170. https://doi.org/10.1016/j.crstbi.2020.08.004

Dai, T., Li, T., Li, R., Zhou, H., Liu, C., Chen, J., & McClements, D. J. (2020). Utilization of plant-based protein-polyphenol complexes to form and stabilize emulsions: Pea proteins and grape seed proanthocyanidins. *Food Chemistry, 329*, Article 127219. https://doi.org/10.1016/j.foodchem.2020.127219

Dai, L., Sun, C., Wei, Y., Mao, L., & Gao, Y. (2018). Characterization of Pickering emulsion gels stabilized by zein/gum Arabic complex colloidal nanoparticles. *Food Hydrocolloids, 74*, 239–248. https://doi.org/10.1016/j.foodhyd.2017.07.040

Dai, L., Zhan, X., Wei, Y., Sun, C., Mao, L., McClements, D. J., & Gao, Y. (2018). Composite zein - propylene glycol alginate particles prepared using solvent evaporation: Characterization and application as Pickering emulsion stabilizers. *Food Hydrocolloids, 85*, 281–290. https://doi.org/10.1016/j.foodhyd.2018.07.013

Destribats, M., Gineste, S., Laurichesse, E., Tanner, H., Leal-Calderon, F., Héroguez, V., & Schmitt, V. (2014). Pickering emulsions: What are the main parameters determining the emulsion type and interfacial properties? *Langmuir, 30*(31), 9313–9326. https://doi.org/10.1021/la501299u

Dickinson, E. (2017). Biopolymer-based particles as stabilizing agents for emulsions and foams. *Food Hydrocolloids, 68*, 219–231. https://doi.org/10.1016/j.foodhyd.2016.06.024

Dixon, M. C. (2008). Quartz crystal microbalance with dissipation monitoring: Enabling real-time characterization of biological materials and their interactions. *Journal of Biomolecular Techniques, 19*(3), 151–158.

Du Le, H., Loveday, S. M., Singh, H., & Sarkar, A. (2020). Pickering emulsions stabilised by hydrophobically modified cellulose nanocrystals: Responsiveness to pH and ionic strength. *Food Hydrocolloids, 99*, Article 105344. https://doi.org/10.1016/j.foodhyd.2019.105344

Du, C.-X., Xu, J.-J., Luo, S.-Z., Li, X.-J., Mu, D.-D., Jiang, S.-T., & Zheng, Z. (2022). Low-oil-phase emulsion gel with antioxidant properties prepared by soybean protein isolate and curcumin composite nanoparticles. *Lebensmittel-Wissenschaft & Technologie, 161*, Article 113346. https://doi.org/10.1016/j.lwt.2022.113346

Erni, P., Fischer, P., Windhab, E. J., Kusnezov, V., Stettin, H., & Läuger, J. (2003). Stress- and strain-controlled measurements of interfacial shear viscosity and viscoelasticity at liquid/liquid and gas/liquid interfaces. *Review of Scientific Instruments, 74*(11), 4916–4924. https://doi.org/10.1063/1.1614433

Falsafi, S. R., Rostamabadi, H., Samborska, K., Mirarab, S., Rashidinejhad, A., & Jafari, S. M. (2022). Protein-polysaccharide interactions for the fabrication of bioactive-loaded nanocarriers: Chemical conjugates and physical complexes. *Pharmacological Research, 178*, Article 106164. https://doi.org/10.1016/j.phrs.2022.106164

Fan, Y., & Wang, Y. (2019). Applications of small-angle X-ray scattering/small-angle neutron scattering and cryogenic transmission electron microscopy to understand self-assembly of surfactants. *Current Opinion in Colloid & Interface Science, 42*, 1–16. https://doi.org/10.1016/j.cocis.2019.02.011

Fauzi, F., Rianjanu, A., Santoso, I., & Triyana, K. (2021). Gas and humidity sensing with quartz crystal microbalance (QCM) coated with graphene-based materials – a mini review. *Sensors and Actuators A: Physical, 330*, Article 112837. https://doi.org/10.1016/j.sna.2021.112837

Fu, D., Deng, S., McClements, D. J., Zhou, L., Zou, L., Yi, J., Liu, C., & Liu, W. (2019). Encapsulation of β-carotene in wheat gluten nanoparticle-xanthan gum-stabilized Pickering emulsions: Enhancement of carotenoid stability and bioaccessibility. *Food Hydrocolloids, 89*, 80–89. https://doi.org/10.1016/j.foodhyd.2018.10.032

Guo, T., Hou, H., Liu, Y., Chen, L., & Zheng, B. (2021). In vitro digestibility and structural control of rice starch-unsaturated fatty acid complexes by high-pressure homogenization. *Carbohydrate Polymers, 256*, Article 117607. https://doi.org/10.1016/j.carbpol.2020.117607

Hosseini, R. S., & Rajaei, A. (2020). Potential Pickering emulsion stabilized with chitosan-stearic acid nanogels incorporating clove essential oil to produce fish-oil-enriched mayonnaise. *Carbohydrate Polymers, 241*, Article 116340. https://doi.org/10.1016/j.carbpol.2020.116340

Hosseini, E., Rajaei, A., Tabatabaei, M., Mohsenifar, A., & Jahanbin, K. (2020). Preparation of pickering flaxseed oil-in-water emulsion stabilized by chitosan-myristic acid nanogels and investigation of its oxidative stability in presence of clove essential oil as antioxidant. *Food Biophysics, 15*(2), 216–228. https://doi.org/10.1007/s11483-019-09612-z

Huang, Z., Liao, L., McClements, D. J., Li, J., Li, R., Zou, Y., Li, M., & Zhou, W. (2022). Utilizing protein-polyphenol molecular interactions to prepare moringa seed residue protein/tannic acid Pickering stabilizers. *Lebensmittel-Wissenschaft & Technologie, 154*, Article 112814. https://doi.org/10.1016/j.lwt.2021.112814

Isa, L., Calzolari, D. C. E., Pontoni, D., Gillich, T., Nelson, A., Zirbs, R., Sánchez-Ferrer, A., Mezzenga, R., & Reimhult, E. (2013). Core–shell nanoparticle monolayers at planar liquid–liquid interfaces: Effects of polymer architecture on the interface microstructure [10.1039/C3SM27367A]. *Soft Matter, 9*(14), 3789–3797. https://doi.org/10.1039/C3SM27367A

Jia, Y., Kong, L., Zhang, B., Fu, X., & Huang, Q. (2022). Fabrication and characterization of Pickering high internal phase emulsions stabilized by debranched starch-capric acid complex nanoparticles. *International Journal of Biological Macromolecules, 207*, 791–800. https://doi.org/10.1016/j.ijbiomac.2022.03.142

Jiang, Y., Chao, G., Zhen, W., Yuting, F., & Xuli, W. (2021). Development of pea protein and high methoxyl pectin colloidal particles stabilized high internal phase pickering emulsions for β-carotene protection and delivery. *Food Hydrocolloids, 113*, Article 106497. https://doi.org/10.1016/j.foodhyd.2020.106497. Article 106497.

Ji, Y., Han, C., Liu, E., Li, X., Meng, X., & Liu, B. (2022). Pickering emulsions stabilized by pea protein isolate-chitosan nanoparticles: Fabrication, characterization and delivery EPA for digestion in vitro and in vivo. *Food Chemistry, 378*, Article 132090. https://doi.org/10.1016/j.foodchem.2022.132090

Ju, M., Zhu, G., Huang, G., Shen, X., Zhang, Y., Jiang, L., & Sui, X. (2020). A novel pickering emulsion produced using soy protein-anthocyanin complex nanoparticles. *Food Hydrocolloids, 99*, Article 105329. https://doi.org/10.1016/j.foodhyd.2019.105329

Karbasi, M., & Askari, G. (2021). Modification of whey protein microgel particles with mono- oligo- and polysaccharides through the Maillard reaction: Effects on structural and techno-functional properties. *Food Structure, 28*, Article 100184. https://doi.org/10.1016/j.foostr.2021.100184

Kuroiwa, T., Kawauchi, Y., Moriyoshi, R., Shino, H., Suzuki, T., Ichikawa, S., Kobayashi, I., Uemura, K., & Kanazawa, A. (2021). Biocompatible homogeneous particle formation via the self-complexation of chitosan with oleic acid and its application as an encapsulation material for a water-insoluble compound. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 624*, Article 126808. https://doi.org/10.1016/j.colsurfa.2021.126808

Larson-Smith, K., Jackson, A., & Pozzo, D. C. (2012). SANS and SAXS analysis of charged nanoparticle adsorption at oil–water interfaces. *Langmuir, 28*(5), 2493–2501. https://doi.org/10.1021/la204513n

Liang, X., Cao, K., Li, W., Li, X., McClements, D. J., & Hu, K. (2021). Tannic acid-fortified zein-pectin nanoparticles: Stability, properties, antioxidant activity, and in vitro digestion. *Food Research International, 145*, Article 110425. https://doi.org/10.1016/j.foodres.2021.110425

Li, R., Dai, T., Tan, Y., Fu, G., Wan, Y., Liu, C., & McClements, D. J. (2020). Fabrication of pea protein-tannic acid complexes: Impact on formation, stability, and digestion of flaxseed oil emulsions. *Food Chemistry, 310*, Article 125828. https://doi.org/10.1016/j.foodchem.2019.125828

Li, M.-F., He, Z.-Y., Li, G.-Y., Zeng, Q.-Z., Su, D.-X., Zhang, J.-L., Wang, Q., Yuan, Y., & He, S. (2019a). The formation and characterization of antioxidant pickering emulsions: Effect of the interactions between gliadin and chitosan. *Food Hydrocolloids, 90*, 482–489. https://doi.org/10.1016/j.foodhyd.2018.12.052

Li, T., Lilja, K., Morris, R. J., & Brandani, G. B. (2019). Langmuir–Blodgett technique for anisotropic colloids: Young investigator perspective. *Journal of Colloid and Interface Science, 540*, 420–438. https://doi.org/10.1016/j.jcis.2019.01.044

Li, M., Ritzoulis, C., Du, Q., Liu, Y., Ding, Y., Liu, W., & Liu, J. (2021). Recent progress on protein-polyphenol complexes: Effect on stability and nutrients delivery of oil-in-water emulsion system [review]. *Frontiers in Nutrition, 8*. https://doi.org/10.3389/fnut.2021.765589

Liu, F., Ma, C., McClements, D. J., & Gao, Y. (2017). A comparative study of covalent and non-covalent interactions between zein and polyphenols in ethanol-water solution. *Food Hydrocolloids, 63*, 625–634. https://doi.org/10.1016/j.foodhyd.2016.09.041

Liu, Y., Shi, Z., Zou, Y., Yu, J., Liu, L., & Fan, Y. (2023). Comparison of cellulose and chitin nanofibers on Pickering emulsion stability—investigation of size and surface wettability contribution. *International Journal of Biological Macromolecules, 235*, Article 123754. https://doi.org/10.1016/j.ijbiomac.2023.123754

Liu, X., Song, Q., Li, X., Chen, Y., Liu, C., Zhu, X., Liu, J., Granato, D., Wang, Y., & Huang, J. (2021). Effects of different dietary polyphenols on conformational changes and functional properties of protein–polyphenol covalent complexes. *Food Chemistry, 361*, Article 130071. https://doi.org/10.1016/j.foodchem.2021.130071

Liu, F., Zheng, J., Huang, C.-H., Tang, C.-H., & Ou, S.-Y. (2018). Pickering high internal phase emulsions stabilized by protein-covered cellulose nanocrystals. *Food Hydrocolloids, 82*, 96–105. https://doi.org/10.1016/j.foodhyd.2018.03.047

Lu, X., & Huang, Q. (2019). Bioaccessibility of polymethoxyflavones encapsulated in resistant starch particle stabilized pickering emulsions: Role of fatty acid complexation and heat treatment [10.1039/C9FO01541H]. *Food & Function, 10*(9), 5969–5980. https://doi.org/10.1039/C9FO01541H

Ma, J.-J., Huang, X.-N., Yin, S.-W., Yu, Y.-G., & Yang, X.-Q. (2021). Bioavailability of quercetin in zein-based colloidal particles-stabilized Pickering emulsions investigated by the in vitro digestion coupled with Caco-2 cell monolayer model. *Food Chemistry, 360*, Article 130152. https://doi.org/10.1016/j.foodchem.2021.130152

Marefati, A., Bertrand, M., Sjöö, M., Dejmek, P., & Rayner, M. (2017). Storage and digestion stability of encapsulated curcumin in emulsions based on starch granule Pickering stabilization. *Food Hydrocolloids, 63*, 309–320. https://doi.org/10.1016/j.foodhyd.2016.08.043

Murai, Y., Shiratori, T., Kumagai, I., Rühs, P. A., & Fischer, P. (2015). Effective viscosity measurement of interfacial bubble and particle layers at high volume fraction. *Flow Measurement and Instrumentation, 41*, 121–128. https://doi.org/10.1016/j.flowmeasinst.2014.10.006

Murray, B. S. (2002). Interfacial rheology of food emulsifiers and proteins. *Current Opinion in Colloid & Interface Science, 7*(5), 426–431. https://doi.org/10.1016/S1359-0294(02)00077-8

Murray, B. S. (2019). Pickering emulsions for food and drinks. *Current Opinion in Food Science, 27*, 57–63. https://doi.org/10.1016/j.cofs.2019.05.004

Murray, B. S., & Dickinson, E. (1996). Interfacial rheology and the dynamic properties of adsorbed films of food proteins and surfactants. *Food Science and Technology International, 2*(3), 131–145. https://doi.org/10.3136/fsti9596t9798.2.131. Tokyo.

Murray, B. S., Ettelaie, R., Sarkar, A., Mackie, A. R., & Dickinson, E. (2021). The perfect hydrocolloid stabilizer: Imagination versus reality. *Food Hydrocolloids, 117*, Article 106696. https://doi.org/10.1016/j.foodhyd.2021.106696

Patel, A. S., Lakshmibalasubramaniam, S., Nayak, B., & Camire, M. E. (2022). Lauric acid adsorbed cellulose nanocrystals retained the physical stability of oil-in-water Pickering emulsion during different dilutions, pH, and storage periods. *Food Hydrocolloids, 124*, Article 107139. https://doi.org/10.1016/j.foodhyd.2021.107139

Pham, L. B., Wang, B., Zisu, B., & Adhikari, B. (2019). Covalent modification of flaxseed protein isolate by phenolic compounds and the structure and functional properties of the adducts. *Food Chemistry, 293*, 463–471. https://doi.org/10.1016/j.foodchem.2019.04.123

Qin, X.-S., Gao, Q.-Y., & Luo, Z.-G. (2021). Enhancing the storage and gastrointestinal passage viability of probiotic powder (Lactobacillus Plantarum) through encapsulation with pickering high internal phase emulsions stabilized with WPI-EGCG covalent conjugate nanoparticles. *Food Hydrocolloids, 116*, Article 106658. https://doi.org/10.1016/j.foodhyd.2021.106658

Quan, T. H., Benjakul, S., Sae-leaw, T., Balange, A. K., & Maqsood, S. (2019). Protein–polyphenol conjugates: Antioxidant property, functionalities and their applications. *Trends in Food Science & Technology, 91*, 507–517. https://doi.org/10.1016/j.tifs.2019.07.049

Ribeiro, E. F., Morell, P., Nicoletti, V. R., Quiles, A., & Hernando, I. (2021). Protein- and polysaccharide-based particles used for Pickering emulsion stabilisation. *Food Hydrocolloids, 119*. https://doi.org/10.1016/j.foodhyd.2021.106839

Sadeghpour, A., Pirolt, F., & Glatter, O. (2013). Submicrometer-sized pickering emulsions stabilized by silica nanoparticles with adsorbed oleic acid. *Langmuir, 29*(20), 6004–6012. https://doi.org/10.1021/la4008685

Sarkar, A., Ademuyiwa, V., Stubley, S., Esa, N. H., Goycoolea, F. M., Qin, X., Gonzalez, F., & Olvera, C. (2018). Pickering emulsions co-stabilized by composite protein/polysaccharide particle-particle interfaces: Impact on in vitro gastric stability. *Food Hydrocolloids, 84*, 282–291. https://doi.org/10.1016/j.foodhyd.2018.06.019

Sarkar, A., & Dickinson, E. (2020). Sustainable food-grade Pickering emulsions stabilized by plant-based particles. *Current Opinion in Colloid & Interface Science, 49*, 69–81. https://doi.org/10.1016/j.cocis.2020.04.004

Sarkar, A., & Mackie, A. R. (2020). Engineering oral delivery of hydrophobic bioactives in real-world scenarios. *Current Opinion in Colloid & Interface Science, 48*, 40–52. https://doi.org/10.1016/j.cocis.2020.03.009

Sarkar, A., Murray, B., Holmes, M., Ettelaie, R., Abdalla, A., & Yang, X. (2016). In vitro digestion of pickering emulsions stabilized by soft whey protein microgel particles: Influence of thermal treatment [10.1039/C5SM02998H]. *Soft Matter, 12*(15), 3558–3569. https://doi.org/10.1039/C5SM02998H

Sarkar, A., Zhang, S., Holmes, M., & Ettelaie, R. (2019). Colloidal aspects of digestion of Pickering emulsions: Experiments and theoretical models of lipid digestion kinetics. *Advances in Colloid and Interface Science, 263*, 195–211. https://doi.org/10.1016/j.cis.2018.10.002

Sengupta, A., Chakraborty, I., G, I., & Mazumder, N. (2022). An insight into the physicochemical characterisation of starch-lipid complex and its importance in food industry. *Food Reviews International, 1–15*. https://doi.org/10.1080/87559129.2021.2021936

Shah, B. R., Li, Y., Jin, W., An, Y., He, L., Li, Z., Xu, W., & Li, B. (2016). Preparation and optimization of Pickering emulsion stabilized by chitosan-tripolyphosphate nanoparticles for curcumin encapsulation. *Food Hydrocolloids, 52*, 369–377. https://doi.org/10.1016/j.foodhyd.2015.07.015

Shah, B. R., Xu, W., & Mráz, J. (2021). Fabrication, stability and rheological properties of zein/chitosan particles stabilized Pickering emulsions with antioxidant activities of the encapsulated vit-D3. *International Journal of Biological Macromolecules, 191*, 803–810. https://doi.org/10.1016/j.ijbiomac.2021.09.159

Su, J., Guo, Q., Chen, Y., Mao, L., Gao, Y., & Yuan, F. (2020). Utilization of β-lactoglobulin- (−)-Epigallocatechin- 3-gallate(EGCG) composite colloidal nanoparticles as stabilizers for lutein pickering emulsion. *Food Hydrocolloids, 98*, Article 105293. https://doi.org/10.1016/j.foodhyd.2019.105293

Su, J., Guo, Q., Yang, S., Li, H., Mao, L., Gao, Y., & Yuan, F. (2021). Electrostatic deposition of polysaccharide onto soft protein colloidal particles: Enhanced rigidity and potential application as Pickering emulsifiers. *Food Hydrocolloids, 110*, Article 106147. https://doi.org/10.1016/j.foodhyd.2020.106147

Sui, X., Sun, H., Qi, B., Zhang, M., Li, Y., & Jiang, L. (2018). Functional and conformational changes to soy proteins accompanying anthocyanins: Focus on covalent and non-covalent interactions. *Food Chemistry, 245*, 871–878. https://doi.org/10.1016/j.foodchem.2017.11.090

Sun, C., Dai, L., & Gao, Y. (2017). Interaction and formation mechanism of binary complex between zein and propylene glycol alginate. *Carbohydrate Polymers, 157*, 1638–1649. https://doi.org/10.1016/j.carbpol.2016.11.046

Tavasoli, S., Liu, Q., & Jafari, S. M. (2022). Development of Pickering emulsions stabilized by hybrid biopolymeric particles/nanoparticles for nutraceutical delivery. *Food Hydrocolloids, 124*, Article 107280. https://doi.org/10.1016/j.foodhyd.2021.107280

Wang, H., Li, M.-F., Lin, F., Su, C.-R., Zeng, Q.-Z., Su, D.-X., He, S., Wang, Q., Zhang, J.-L., & Yuan, Y. (2021). Fabrication and characterization of bi-crosslinking Pickering emulsions stabilized by gliadin/alginate coacervate particles. *Journal of Food Engineering, 291*, Article 110318. https://doi.org/10.1016/j.jfoodeng.2020.110318

Wei, Y., Guo, A., Liu, Z., Mao, L., Yuan, F., Gao, Y., & Mackie, A. (2021). Structural design of zein-cellulose nanocrystals core–shell microparticles for delivery of curcumin. *Food Chemistry, 357*, Article 129849. https://doi.org/10.1016/j.foodchem.2021.129849

Wei, Y., Liu, Z., Guo, A., Mackie, A., Zhang, L., Liao, W., Mao, L., Yuan, F., & Gao, Y. (2021). Zein colloidal particles and cellulose nanocrystals synergistic stabilization of pickering emulsions for delivery of β-carotene. *Journal of Agricultural and Food Chemistry, 69*(41), 12278–12294. https://doi.org/10.1021/acs.jafc.0c07800

Wei, Y., Zhang, L., Liao, W., Mao, L., Zhang, M., Guo, X., Huang, C., Han, H., Mackie, A., & Gao, Y. (2021). Enhanced stability and controlled gastrointestinal digestion of β-carotene loaded Pickering emulsions with particle–particle complex interfaces [10.1039/D1FO01714D]. *Food & Function, 12*(21), 10842–10861. https://doi.org/10.1039/D1FO01714D

Wijaya, W., Turan, S., Setiowati, A. D., Dewettinck, K., Patel, A. R., & Van der Meeren, P. (2020). Effect of low-methoxy pectin on interfacial and emulsion stabilizing properties of heated whey protein isolate (WPI) aggregates. *Food Structure, 26*, Article 100159. https://doi.org/10.1016/j.foostr.2020.100159

Xu, F., Liamas, E., Bryant, M., Adedeji, A. F., Andablo-Reyes, E., Castronovo, M., Ettelaie, R., Charpentier, T. V. J., & Sarkar, A. (2020). A self-assembled binary protein model explains high-performance salivary lubrication from macro to nanoscale. *Advanced Materials Interfaces, 7*(1), Article 1901549. https://doi.org/10.1002/admi.201901549

Xu, Y., Wei, Z., Xue, C., & Huang, Q. (2022). Assembly of zein–polyphenol conjugates via carbodiimide method: Evaluation of physicochemical and functional properties. *Lebensmittel-Wissenschaft & Technologie, 154*, Article 112708. https://doi.org/10.1016/j.lwt.2021.112708

Xu, H., Zhang, T., Lu, Y., Lin, X., Hu, X., Liu, L., He, Z., & Wu, X. (2019). Effect of chlorogenic acid covalent conjugation on the allergenicity, digestibility and functional properties of whey protein. *Food Chemistry, 298*, Article 125024. https://doi.org/10.1016/j.foodchem.2019.125024

Yan, H., Chen, X., Shi, J., Shi, Z., Sun, W., Lin, Q., Wang, X., & Dai, Z. (2017). Fabrication and evaluation of chitosan/NaYF4:Yb3+/Tm3+ upconversion nanoparticles composite beads based on the gelling of Pickering emulsion droplets. *Materials Science and Engineering: C, 71*, 51–59. https://doi.org/10.1016/j.msec.2016.09.066

Yan, X., Diao, M., Li, C., Lu, C., Zhao, P., & Zhang, T. (2022). Formation and properties of starch-palmitic acid complex nanoparticles and their influence on Pickering emulsions. *International Journal of Biological Macromolecules*. https://doi.org/10.1016/j.ijbiomac.2022.01.170

Yang, H., Su, Z., Meng, X., Zhang, X., Kennedy, J. F., & Liu, B. (2020). Fabrication and characterization of Pickering emulsion stabilized by soy protein isolate-chitosan nanoparticles. *Carbohydrate Polymers, 247*, Article 116712. https://doi.org/10.1016/j.carbpol.2020.116712

Yan, X., Kou, L., Wei, H., Ren, L., & Zhou, J. (2020). Effect of fatty acid addition on properties of amylose nanoparticles prepared via complexing and precipitation. *Industrial Crops and Products, 145*, Article 112097. https://doi.org/10.1016/j.indcrop.2020.112097

Zembyla, M., Lazidis, A., Murray, B. S., & Sarkar, A. (2019). Water-in-Oil pickering emulsions stabilized by synergistic particle–particle interactions. *Langmuir, 35*(40), 13078–13089. https://doi.org/10.1021/acs.langmuir.9b02026

Zembyla, M., Liamas, E., Andablo-Reyes, E., Gu, K., Krop, E. M., Kew, B., & Sarkar, A. (2021). Surface adsorption and lubrication properties of plant and dairy proteins: A comparative study. *Food Hydrocolloids, 111*, Article 106364. https://doi.org/10.1016/j.foodhyd.2020.106364

Zembyla, M., Murray, B. S., & Sarkar, A. (2018). Water-in-oil pickering emulsions stabilized by water-insoluble polyphenol crystals. *Langmuir, 34*(34), 10001–10011. https://doi.org/10.1021/acs.langmuir.8b01438

Zhang, S., Murray, B. S., Suriyachay, N., Holmes, M., Ettelaie, R., & Sarkar, A. (2021). Synergistic interactions of plant protein microgels and cellulose nanocrystals at the interface and their inhibition of the gastric digestion of pickering emulsions. *Langmuir, 37*(2), 827–840. https://doi.org/10.1021/acs.langmuir.0c03148

Zhang, X., Wu, Y., Li, Y., Li, B., Pei, Y., & Liu, S. (2022). Effects of the interaction between bacterial cellulose and soy protein isolate on the oil-water interface on the digestion of the Pickering emulsions. *Food Hydrocolloids, 126*, Article 107480. https://doi.org/10.1016/j.foodhyd.2021.107480

Zhang, Q., Yue, W., Zhao, D., Chen, L., Xu, Z., Lin, D., & Qin, W. (2022a). Preparation and characterization of soybean protein isolate-dextran conjugate-based nanogels. *Food Chemistry, 384*, Article 132556. https://doi.org/10.1016/j.foodchem.2022.132556

Zhou, B., Gao, S., Li, X., Liang, H., & Li, S. (2020). Antioxidant Pickering emulsions stabilised by zein/tannic acid colloidal particles with low concentration. *International Journal of Food Science and Technology, 55*(5), 1924–1934. https://doi.org/10.1111/ijfs.14419

Zhou, F.-Z., Huang, X.-N., Wu, Z.-l., Yin, S.-W., Zhu, J.-h., Tang, C.-H., & Yang, X.-Q. (2018a). Fabrication of zein/pectin hybrid particle-stabilized pickering high internal phase emulsions with robust and ordered interface architecture. *Journal of Agricultural and Food Chemistry, 66*(42), 11113–11123. https://doi.org/10.1021/acs.jafc.8b03714

Zhou, F.-Z., Yan, L., Yin, S.-W., Tang, C.-H., & Yang, X.-Q. (2018). Development of pickering emulsions stabilized by gliadin/proanthocyanidins hybrid particles (GPHPs) and the fate of lipid oxidation and digestion. *Journal of Agricultural and Food Chemistry, 66*(6), 1461–1471. https://doi.org/10.1021/acs.jafc.7b05261

Zhu, C.-P., Zhang, H.-H., Huang, G.-Q., & Xiao, J.-X. (2021). Whey protein isolate—low methoxyl pectin coacervates as a high internal phase Pickering emulsion stabilizer. *Journal of Dispersion Science and Technology, 42*(7), 1009–1020. https://doi.org/10.1080/01932691.2020.1724801

Zou, Y., Yang, X., & Scholten, E. (2019). Tuning particle properties to control rheological behavior of high internal phase emulsion gels stabilized by zein/tannic acid complex particles. *Food Hydrocolloids, 89*, 163–170. https://doi.org/10.1016/j.foodhyd.2018.10.037