Oxidative stability of Pickering emulsions

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A B S T R A C T

In recent years, Pickering emulsions have been the focus of growing interest because of their possible role as alternatives to conventional emulsions. Some reviews have investigated the physical stability of Pickering emulsions, but the oxidative stability of these emulsions remains largely unexplored. In this review, the oxidation mechanism and factors affecting lipid oxidation rates in Pickering emulsions are discussed. Then, different food-grade solid particles are evaluated for their ability to stabilize Pickering emulsions. Finally, several strategies are reviewed for improving the oxidative stability of Pickering emulsions. These strategies are based on efforts to manipulate the physical and chemical properties of the interfacial layer, increase the concentration of antioxidants at the interfacial layer through incorporating them into solid particles, cause oil droplets to crowd at high packing fractions, trap oil droplets in a gel network and increase the viscosity of the continuous phase.

1. Introduction

Emulsion science is a subdivision of the larger field of colloid science, which is concentrated on the synthesis and use of particulate laden fluids. Simple emulsions are: oil-in-water (O/W) emulsions and water-in-oil (W/O) emulsions. O/W emulsions are among the dispersion structures commonly used in foodstuffs. Emulsions are stabilized with emulsifiers and surfactants that reduce surface tension and coat the surface of the droplets. There are a range of natural and synthetic materials that promote the long-term stability of emulsions (Dutta, Knowlton & Blair, 2016). Pickering emulsions are a group of emulsions which are stabilized by solid particles that adsorb onto the interface of emulsions due to their appropriate wettability (Chevalier & Bolzinger, 2013). Solid particles can stabilize various types of emulsions: O/W, W/O, water-in-water (W/W), oil-in-oil (O/O), water-in-oil-in-water (W/O/W), oil-in-water-in-oil (O/W/O), and (oil-in-oil-in-oil) O/O/O.

According to Scopus search results, from 2010 to 2020, the ratio of picking emulsion studies to total emulsion studies has increased (from 1.8% to 9%) (Fig. 1). This reinstates the significance of attractive properties of Pickering emulsions in comparison with conventional ones. The differences between Pickering emulsions and conventional emulsions are: unlike conventional emulsions, in Pickering emulsions the solid particles need not be amphiphilic, but they must have good wettability with both of aqueous phase and oil phase to make stable docking, Pickering emulsions provide more thickness and surface load than conventional emulsions, and in Pickering emulsions unlike

conventional emulsions there is no emulsifier dynamic exchange at the interface (Mukherjee, 2020; Jafari, Doost, Nasrabadi, Boostani, & Van der Meeren, 2020). Pickering emulsions display very high physical stability (sometimes up to several years (Marefati & Rayner, 2020)) due to the irreversible adsorption of solid particles at the oil–water interface. This usually results in a densely packed particle layer which can prevent coalescence or flocculation by inducing a steric barrier and by reducing the rate of sedimentation or creaming. This irreversible adsorption of solid particles is effective in contrast to the behavior of surfactant molecules which are usually in rapid dynamic equilibrium between the oil–water interface and the bulk phases. Unlike emulsions stabilized by a single surfactant type, Pickering emulsions can be inverted from W/O to O/W simply by increasing the volume fraction of the water. For surfactant systems, this behavior occurs only when a combination of surfactants is used. Pickering emulsions are most stable when being close to this inversion point, thereby being in complete contrast to those that are made using surfactants where stability is least found. Also, Pickering emulsions can adjust to their applications because of the very large number of possible combinations that various types of particles can have, along with aqueous and oily phases in use (Albert et al., 2019; Ortiz, Pochat-Bohatier, Cambedouzou, Bechelany, & Miele, 2020). Furthermore, Pickering emulsions have several potential uses in food applications, for example as an encapsulation agent (to protect bioactive ingredients and enhance nutritional value), fat alternatives for making low fat products, and preparation of bread without additives (Jafari et al., 2020). Despite the numerous advantages of Pickering emulsions,

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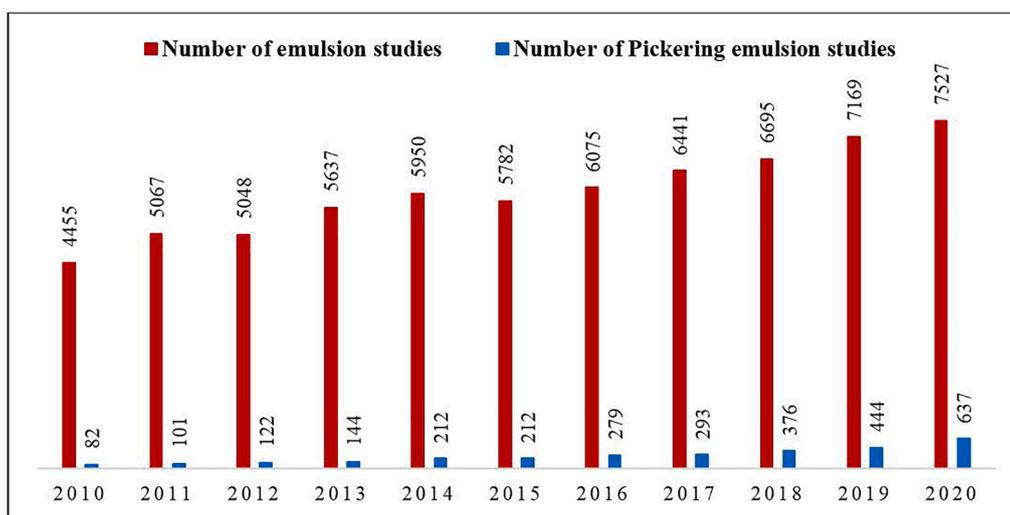 *E-mail address:* golmakani@shirazu.ac.ir (M.-T. Golmakani).

Fig. 1. Publications on Pickering emulsions among all publications on emulsions by the keywords "emulsion" and "Pickering emulsion". The source of information was Scopus database (keywords searched in the title, abstract and keywords).

one of the crucial factors that can deteriorate their quality during storage is lipid oxidation (Liu, Bhattarai, Mikkonen, & Heinonen, 2019a; Aveyard, Binks & Clint, 2003).

Lipid oxidation describes a complex reaction between unsaturated fatty acyl groups with active oxygen species (Chen, McClements, & Decker, 2013). Lipid oxidation in O/W emulsions primarily occurs at the oil–water interface, which is due to the fact that the interface of oil–water is the contact region between pro-oxidant compounds (such as transition metal ions) which is dissolved in the aqueous phase and unsaturated lipids (located in the emulsion droplets). Accordingly, the interface properties are important factors (physical and chemical properties) in controlling lipid oxidation in O/W emulsions (McClements & Decker, 2000). Besides, some solid particles create physical and chemical barriers according to their characteristics and effectively improve the oxidative stability of O/W emulsions (Espinal-Ruiz, Restrepo-Sánchez, Narváez-Cuenca, & McClements, 2016; Torcello-Gómez & Foster, 2016; Zhou, Gao, Li, Liang, & Li, 2019). Oxidative stability in Pickering emulsions has been suggested to be higher than conventional emulsions. In Pickering emulsions can use the particles with good properties at the interface such as: create a thicker interface, intrinsic antioxidant ability and create a positive droplet surface load, so higher oxidative stability can be achieved by carefully selecting the particles used (repel positively charged pro-oxidants such as iron) (Mwangi, Lim, Low, Tey, & Chan, 2020). The oxidative stability of Pickering emulsions can be promoted by manipulating the properties of interfacial layers (such as by increasing the thickness, antioxidant activity, charge, and selective surfactants).

Most of the relevant reviews on Pickering emulsions have concentrated on the fabrication, physical stability, and applications of Pickering emulsions but, as far as we know, chemical stability with regard to the lipid oxidation of Pickering emulsions is largely undiscovered. Oxidative stability tests of Pickering emulsions which are stabilized by solid particles are shown in Table 1 as follows: lipid hydroperoxides, peroxide, TBARS, *p*-anisidine, malondialdehyde, and acid values as well as conjugated dienes, hexanal, 2-octenal, 2-heptenal, 2-pentenal, 2-pentylfuran, 2,4-heptadienal, 2-hexenal, heptanal, and oxygen consumption. In this study, first, different compounds that can be used as food-grade solid particles for producing Pickering emulsions have been categorized. Then, the mechanism of lipid oxidation and factors affecting lipid oxidation in Pickering emulsion have been discussed. Finally, strategies for improving the oxidative stability of these emulsions have been reviewed.

2. Mechanism of lipid oxidation in Pickering O/W emulsions

The auto-oxidation process can be divided into three stages, i.e. initiation, propagation, and termination. The mechanism of lipid oxidation in O/W emulsions differs from bulk oils. This phenomenon is due to the presence of an aqueous phase containing antioxidants and pro-oxidants as well as an oil–water interface which usually affect interactions between the oil phase and compounds present in the water phase (Berton- Carabin, Ropers, & Genot, 2014). Generally, for a specific oil, the lipid oxidation rate in O/W emulsion is higher than the bulk oil. This fact is due to the presence of the interfacial area between the aqueous phase and the oil phase, which can promote the reaction between transition metal ions present in the aqueous phase and unsaturated fatty acids (Frankel, Huang, Kanner, & German, 1994; McClements & Decker, 2000). A schematic representation of lipid oxidation reaction at the interfacial layer of Pickering emulsions is presented in Fig. 2. The reaction between transition metal ions dissolved in the aqueous phase and hydroperoxides located at oil–water interface is one of the most important mechanisms in the oxidation of O/W emulsions. This reaction increases the dissociation of lipid hydroperoxides into alkoxy and peroxyl radicals, which further increases the lipid oxidation rate. The interfacial area in O/W emulsions could also encourage the oil phase to have accessibility of oxygen as it is dissolved in the aqueous phase. This can be an important factor when the oxygen is initially dissolved in the oil phase and has been consumed. Furthermore, the process of emulsification itself could increase the rate of lipid oxidation through incorporation of oxygen, thereby overheating due to shear stress (Mao, Xu, Yang, Yuan, Gao, & Zhao, 2009) and the formation of free radicals through acoustic cavitation if sonication is applied (Jana, Agarwal, & Chatterjee, 1990).

2.1. Factors influencing on lipid oxidation rate in Pickering O/W emulsions

2.1.1. Interfacial layer properties

Several compounds that are solubilized in the aqueous phase include oxygen, transition metal ions and water-soluble antioxidants. The interfacial layer is the region where unsaturated fatty acids in the oil phase and the compounds solubilized in the aqueous phase come into close proximity. Thus, the interfacial layer plays an important role in determining the lipid oxidation rate in food emulsions (Hu, McClements, & Decker, 2003a).

Table 1
Selected examples of solid Particles that have been used for improving oxidative stability of Pickering emulsions.

Solid particles	Oil type	Results	Oxidation test	Usage level	Reference
Protein					
Corn-peptide-functionalized calcium phosphate particles	Algal oil	Improved oxidative stability and flavor properties	PV*	1.28% in aqueous phase of emulsion with water:oil ratio of 4:6	Ruan et al. (2018)
Kafirin nanoparticles	Sunflower oil	Retarded lipid oxidation rate	PV and TBARS value	1% (w/v) in emulsion with water:oil ratios of 8:2, 6:4, 4:6, and 2:8	Xiao et al. (2015)
Polysaccharide					
Microcrystalline cellulose-modified starch	Sunflower oil	Reduced lipid oxidation rate	PV and AV	0.1–2.5% (w/w) in emulsion	Kargar et al. (2012)
Cellulose nanocrystals	Rice bran oil	Exhibited the highest oxidative stability	PV	0.25–1% (w/w) in aqueous phase of W/O emulsion with water:oil ratio of 1:1	Angkuratipakorn et al. (2017)
Chitosan-myristic acid nanogels	Flaxseed oil	Prevented lipid oxidation	PV and TBARS value	Different myristic acid:chitosan ratios (0:1, 0.25:1, 0.5:1, and 0.75:1) in oil:nanogel ratio of 10:1 (5% O/W emulsion)	Hosseini et al. (2019)
Chitosan-stearic acid nanogel	Sunflower oil	Increased oxidative stability	PV and TBARS value	Different stearic acid:chitosan ratios (0:1, 0.25:1, 0.5:1, and 0.75:1) in oil:nanogel ratio of 20:1 (10% O/W emulsion)	Atarian et al. (2019)
Modified cyclodextrin carotene inclusion complex	Linseed oil	Improved oxidative stability	PV and TBARS value	2 g in 68 g aqueous phase in emulsion with oil:water ratio of 30:68	Niu et al. (2019)
Chitosan hydrochloride/ carboxymethyl starch complex nanogels	Corn oil	Delayed lipid oxidation rate	PV and TBARs value	1.5% (w/v) in O/W emulsion	Li et al. (2020)
Starch particles	Freshly refined sunflower oil	Decreased oxidation rate	PV and acid value	1% and 2% (w/w) in O/W emulsion	Song et al. (2020)
Lipid particle					
SLNs (glyceryl stearyl citrate)	Canola oil	Stabilized a model food grade O/W emulsion for at least 12 weeks		7.5% (w/w) in aqueous phase of O/W emulsion with oil:water ratio of 2:8	Gupta & Rousseau (2012)
Tripalmitin	Sunflower oil	Provided a mechanical barrier against coalescence		4% (w/w) in O/W emulsion and 1% (w/w) in W/O emulsion	Pawlik et al. (2016)
CLPs (solid tripalmitin and liquid tricaprylin)	Sunflower oil	Influenced particle adsorption and emulsion structure, and leaded to emulsions with remarkable physical stability		1% (w/w) in aqueous phase in O/W emulsion with oil:water ratio of 1:9	Schröder et al. (2017)
Microcrystalline glyceryl tristearate and cetyl palmitate	Sunflower oil	Exhibited tailorable microstructural attributes and established as drivers of Pickering functionality		2.5% (w/w) microcrystalline glyceryl tristearate and 2.5% (w/w) cetyl palmitate in O/W emulsion	Zafeiri et al. (2017)
CLPs (tripalmitin)	Sunflower oil	Destabilized emulsion at low surface coverage and stabilized emulsion at higher surface coverage		5% (w/w) in aqueous phase of O/W emulsion with oil:water ratio of 1:9	Schröder et al. (2018)
SLNs (glyceryl tristearate)	Medium-chain triglyceride oil	Increased physical stability of emulsions		10% (v/v) in O/W emulsion	Milsmann et al. (2018)
Protein-polysaccharide complex					
Zein-chitosan complex particles/electrostatic	Corn oil	Enhanced oxidative stability	PV, TBARs value and hexanal measurement	7% zein and 0.35% chitosan in aqueous phase of O/W emulsion with oil:water ratio of 1:1	Wang et al. (2015)
Gliadin-chitosan hybrid particles/HIPE	Corn oil	Decreased LH & MDA	PV and TBARS value	0.2–2% gliadin and 0.1% chitosan in aqueous phase of O/W emulsion with different oil:water ratios	Zeng et al. (2017)
Zein-Pectin hybrid particles/HIPE	Commercial corn oil	Enhanced oxidation/ storage stability	PV and TBARS value	0.02% in aqueous phase of emulsion with oil:water ratio of 8:2	Zhou et al. (2018a)
Chitosan-caseinophosphopeptides nanocomplexes/HIPE	Corn and linseed oils	Decreased oxidation rate	PV and TBARS value	0.3% (w/w) chitosan in aqueous phase of emulsion with oil:water ratio of 8:2 (chitosan:caseinophosphopeptides ratios of 6:0, 6:1, 6:2, 6:3, 6:4, 6:5, and 6:6)	Huang et al. (2019)
Gliadin-chitosan/ complex coacervate	Corn oil	Stabilized Pickering emulsion	PV	2.0% (w/v) gliadin and 0.1% (w/v) chitosan in O/W emulsion	Li et al. (2019)
Faba bean protein isolate-chitosan/soluble complex	Rapeseed oil	Improve oxidative and physical stability of emulsion	CD, hexanal, 2-octenal, 2-heptenal, 2-pentenal, 2-pentylfuran, 2,4-heptadienal, 2-hexenal, and heptanal measurement	1% (w/v) faba bean protein isolate and 0.1% (w/v) chitosan in O/W emulsion	Liu et al. (2020)
Zein-pectin gel like shell structure/electrostatic	Corn germ oil		TBARS value	1% (w/v) in O/W emulsion	Jiang et al. (2020)

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Table 1 (*continued*)

Solid particles	Oil type	Results	Oxidation test	Usage level	Reference
Cellulose nanofibrils (bacterial cellulose)-soy protein isolate nanoparticles/ electrostatic	Canola oil	Protected intrinsic lipid oxidation of Pickering emulsion Improved oxidative stability and anti-digestibility	PV and TBARS value	1.0%, 1.5%, 2.0%, 2.5%, and 3.0% soy protein isolate in O/W emulsion with soy protein isolate:cellulose weight ratio of 12.5:1	Zhang et al. (2019)
Flaxseed protein-mucilage/ electrostatic	Flaxseed oil	Increased oxidative stability	PV and TBARs value	5 mg/mL in O/W emulsion	Nasrabadi et al. (2019)
Protein-polyphenol complex Flaxseed protein isolate /flaxseed polyphenols	Flaxseed oil	Improved interfacial and emulsifying ability of protein and increased oxidative stability	PV and TBARS value	4.5% (w/v) in O/W emulsion	Pham et al. (2019)
Proline-rich gliadin/ proanthocyanidins	Corn oil	Formed antioxidant particles as a barrier against lipid oxidation	TBARs value and Hexanal and oxygen consumption	0.5% gliadin in aqueous phase of emulsion with oil:water ratio of 1:1 (proanthocyanidins:gliadin mass ratios of 0, 1%, 2%, 5%, and 10%)	Zhou et al. (2018b)
Zein/tannic acid	Corn oil	Formed layer-by-layer interfacial architecture on oil − water surface by noncovalent interaction	PV	0.1%, 0.2%, and 0.3% (w/v)zein in aqueous phase of emulsions with oil:water ratios of 4:1 to 1:1 (zein:tannic acid ratios of 4:1, 2:1, and 1:1)	Zou et al. (2015)Zou et al. (2017)Zhou et al. (2019)
Soy protein isolate/ anthocyanins	Soy oil	Improved oxidative stability and resistance to *in vitro* digestion	PV and TBARs value	6% (w/v) soy protein isolate solution and 0, 0.05%, 0.10%, and 0.15% (v/v) anthocyanins in O/W emulsion	Ju et al. (2020)
Zein nanoparticles/gallic acid	Stripped corn oil	Improved oxidative stability	PV	0, 0.25%, 0.5%, 1%, and 2 % zein and 0.5 mM gallic acid in O/W emulsion	Zhao et al. (2020)
Whey protein/rutin	Sunflower oil	Stabilized emulsions both against creaming and oil oxidation	PV and TBARS value	1.5% whey protein and 1 mM rutin in aqueous phase of emulsion with oil:water ratio of 1:4	Atarés et al. (2012)
Rice protein isolate/ferulic acid	Corn oil	Improved oxidative stability	PV, TBARS value, and Hexanal measurement	1% rice protein isolate with different concentrations of ferulic acid solutions: 0, 0.5, 1, 5,10, 20, and 40 μg/mL in the aqueous phase of emulsion with oil:water ratio of 1:9	Jia et al. (2019)

* PV = peroxide value; TBARS = thiobarbituric acid reactive substances value; CD = conjugated diene; AV = *p*-Anisidine value; SLN = solid lipid nanoparticle, CLN = colloidal lipid nanoparticle; HIPE = high internal phase emulsion.
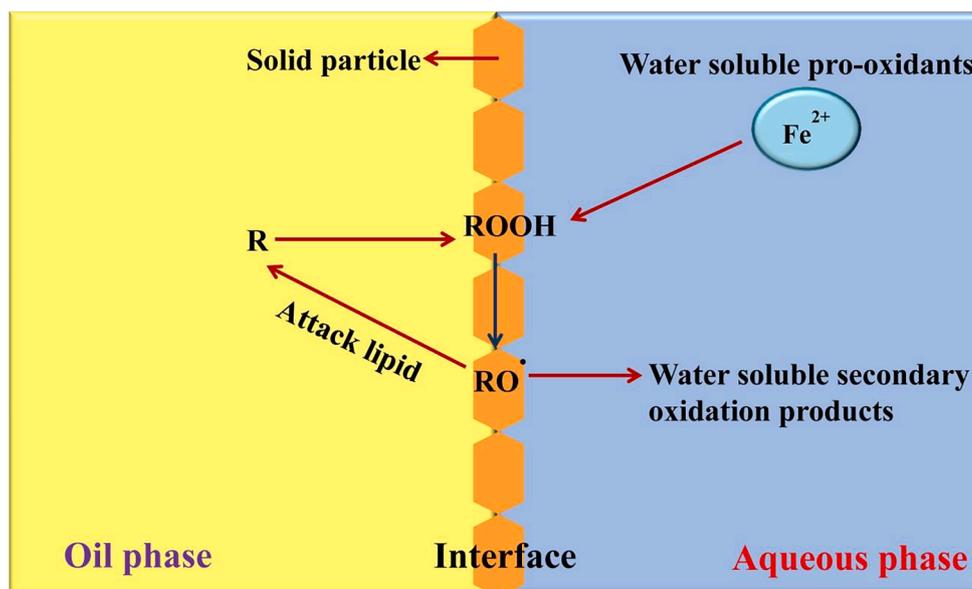

Fig. 2. Mechanism of lipid oxidation in Pickering oil-in-water emulsion (R = unsaturated fatty acid, ROOH = fatty acid peroxide, RO• = alkoxy radical).

2.1.1.1. Physical properties. The physical properties of an interface can influence the diffusion of pro-oxidants, free radicals, and oxygen through the interfacial layer (McClements & Decker, 2000). The thickness of interfaces, as formed by solid particles, is about 10–100 nm, whereas small molecule emulsifiers and biopolymers may form interfacial layers with about 1 nm and 1–50 nm thickness, respectively (McClements, Bai, & Chung, 2017). The thickness of the interfacial layer can influence the accessibility of water-soluble transition metal ions to the oil phase (Berton-Carabin, Ropers & Genot, 2014). Also, the thickness of the interfacial layer can influence the location and mass transfer
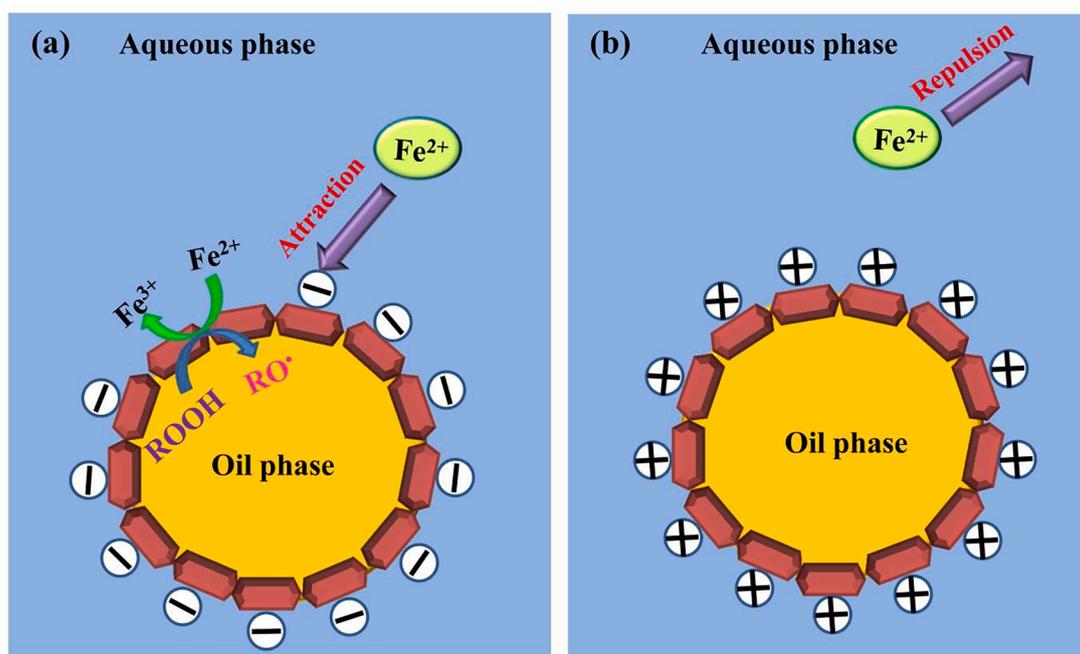
Fig. 3. Effect of (a) negative and (b) positive electrical charge of the interfacial layer on lipid oxidation in Pickering emulsion (ROOH = fatty acid peroxide, RO$^\bullet$ = alkoxy radical).

of lipid hydroperoxides, antioxidants, and free radicals. Furthermore, the thickness of the interfacial layer can influence the diffusion of the oxygen molecules to attack the oil droplets (Dai et al., 2018). The size of the solid particles can affect the thickness of the interfacial layer (Hu, McClements, & Decker, 2003b). In this regard, Kargar, Fayazmanesh, Alavi, Spyropoulos and Norton (2012) stated that microcrystalline cellulose particles can create a thicker interfacial layer around the oil droplets in comparison with the modified starch particles due to the larger particle size of microcrystalline cellulose (415 nm), as compared to modified starch particles (120 nm). They observed that the emulsions that had been stabilized by microcrystalline cellulose particles showed lower peroxide value (primary oxidation products) and *p*-anisidine value (secondary oxidation products) than those emulsions stabilized by modified starch particles during 7 days of storage at 40 °C.

While thickness is a partial cause of the antioxidant effect, the interfacial layer may actually occur in response to the relevant properties that generate the interfacial layer. Also, it can change when the thickness of the interfacial layer is altered. For example, changing the thickness of the interfacial layer may result in a change of the total amount of antioxidant groups present in the interfacial layer (Dai et al., 2018).

Permeability of the interfacial layer is another important physical property of interfacial layers that can influence the ability to retard or promote lipid oxidation rates. This parameter corresponds with the gathering of the molecules in and around the interface (Pan, Tikekar, & Nitin, 2013). The interfacial layer can inhibit the permeation of pro-oxidant compounds when it contains very small pores that cannot allow pro-oxidant compounds to pass through. Similarly, when the interfacial layer contains constituents that strongly bind or repel the pro-oxidant compounds, it can inhibit their permeation (Dai et al., 2018).

2.1.1.2. Chemical properties. The chemical constituents of solid particles which can scavenge free radicals or chelate transition metal ions can influence lipid oxidation in Pickering emulsions (Hu et al., 2003b). Phenolic compounds which are active on the surface can be used as antioxidant solid particles for the stabilization of Pickering emulsions. Noon, Mills, and Norton (2020) investigated the application of antioxidant rutin hydrate solid particles in comparison with conventional

emulsifiers, namely, sodium dodecyl sulphate, whey protein isolate, and polysorbate 20 in an effort to inhibit lipid oxidation in O/W emulsions. They observed that the emulsion stabilized by rutin hydrate exhibited lower peroxide value and *p*-anisidine value than those emulsions stabilized by sodium dodecyl sulphate and polysorbate 20 without the addition of ferrous iron during 7 days of storage at 40 °C. However, rutin hydrate showed pro-oxidant activity in the presence of ferrous iron. Also, they stated that a lower efficiency of rutin hydrate than whey protein isolate may result from the fact that rutin hydrate particles are not able to create a continuous 'shell' to act as a barrier around oil droplets. This is cited in contrast to whey protein isolate. Accordingly, a major challenge in using phenolic compounds as solid particles, with the aim of stabilizing Pickering emulsions, is to produce them in suitable form and in enough quantity, whereby they can play the role of an effective interfacial barrier.

Also, proteins that contain methionine, tryptophan, and cysteine amino acids exhibit significant antioxidant activity due to the free radical scavenging activity of these amino acids. Cysteine and tryptophan oxidation was observed in emulsions containing β-lactoglobulin throughout the course of study. It was observed that the majority of loss in free sulfhydryl and tryptophan occurred while lipid oxidation was in a lag period. The depletion of cysteine and tryptophan, which preceded the onset of lipid oxidation, suggests that these residues act as free radical scavengers (Elias, McClements, & Decker, 2005). Levine, Mosoni, Berlett, and Stadtman (1996) observed that the surface-exposed methionine residues of glutamine synthetase were oxidized within a range of hydrogen peroxide concentrations between 5 and 160 mM, showing that these amino acids are free radical scavengers. The Pickering emulsion of high internal phase emulsion (HIPE) stabilized by gliadin/chitosan complex particles was more effective than its corresponding bulk oil in reducing peroxide values and thiobarbituric acid reactive substances during 14 days of storage at 37 °C. Besides, the fact that the interfacial layer based on the complex particles acts as an effective physical barrier, the presence of amino acids in side chains of gliadin with antioxidant capacity can reduce lipid oxidation (Zeng et al., 2017). Some polysaccharides also have the capacity to inactive free radicals. Jiang et al. (2020) reported that pectin from hawthorn wine pomace exhibited higher radical scavenging activity than commercial
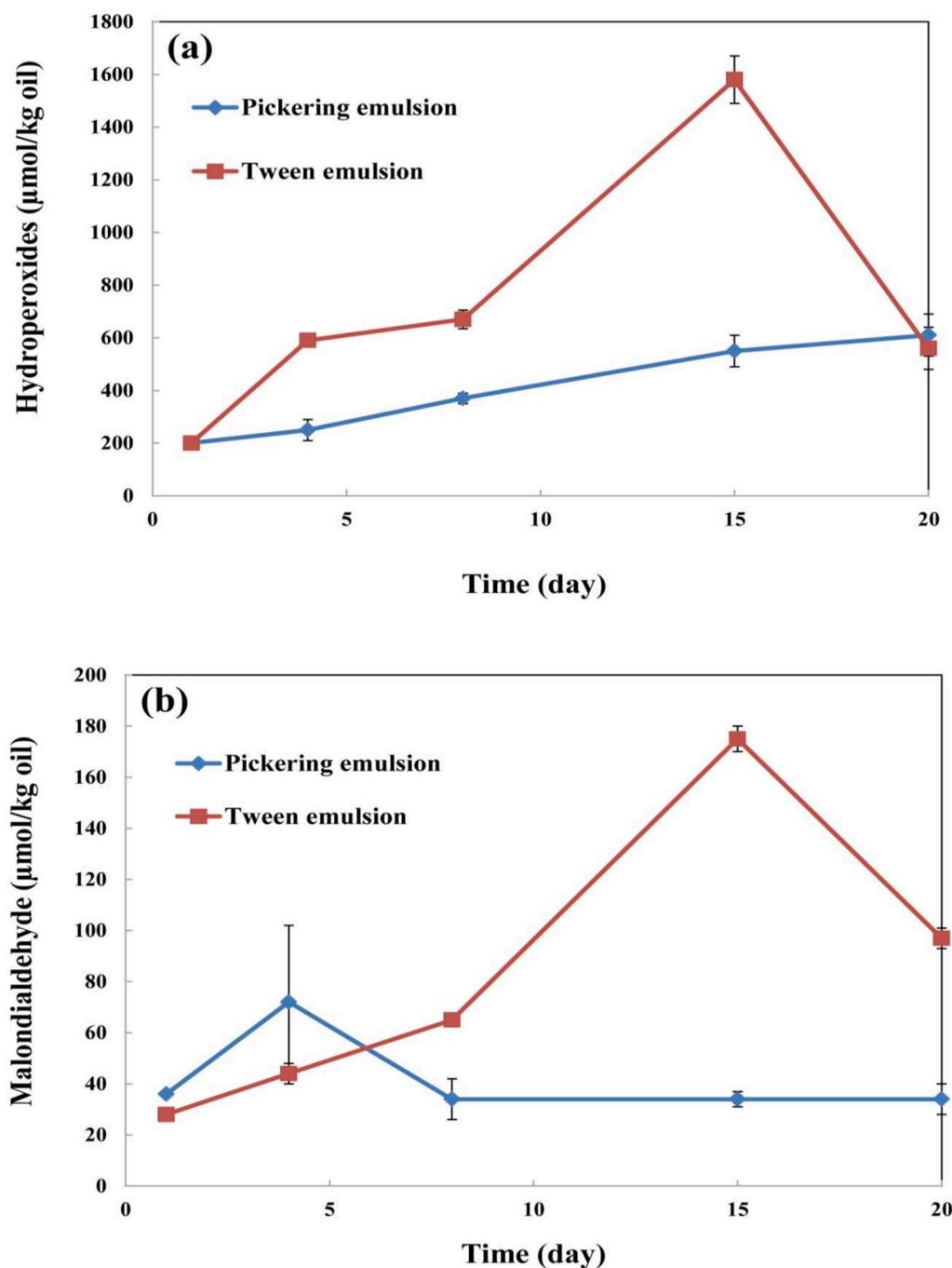
Fig. 4. Formation of (a) hydroperoxides and (b) malondialdehyde in Pickering emulsion stabilized by chitosan-stearic acid nanogel in comparison with emulsion stabilized by Tween 80 (Atarian et al. (2019).

apple pectin and citrus pectin. They stated that the higher radical scavenging activity of pectin from hawthorn wine pomace might be due to the lower molecular weight of pectin from hawthorn wine pomace than those of commercial apple and citrus pectins. Previous studies have shown that within a certain molecular weight range, the molecular weight of polysaccharides is inversely related to the biological activity of the polysaccharides (Ogutu & Mu, 2017; Wang et al., 2016; Xia, Liu, Zhang, & Chen, 2011). In addition, small molecules of residual antioxidants in extracted hawthorn wine pomace pectin may also be responsible for its strong radical scavenging activity during the purification procedure (Jiang et al., 2020).

2.1.1.3. Electrical charge. The electrical charge of emulsion droplets can

have an impact on the removal and absorption of transition metal ions (Fig. 3). Atarian, Rajaei, Tabatabaei, Mohsenifar, and Bodaghi (2019) stated that a lower oxidation rate of emulsion stabilized by chitosan-stearic acid nanogels than emulsions stabilized by Tween 80 may be due to the positive charge of the interfacial layer in emulsions stabilized by chitosan-stearic acid, which can repel the transition metal ions from the interface (Fig. 4). In contrast, a negative charge can increase lipid oxidation via attracting the transition metal ions to the interface (Dai et al., 2018).

Several studies have reported that the pH of the emulsions stabilized by solid particles based on proteins can influence lipid oxidation rate by altering the charge of the proteins (Zhu et al., 2018). In this regard, the lipid oxidation rate was faster when the pH was higher than the

isoelectric point of the protein and the charge of the interfacial layer was negative. Accordingly, solid particles based on proteins can exhibit pro-oxidant activity at high pH values, but can exhibit antioxidant activity at low pH values (Dai et al., 2018).

2.1.2. Droplet size

The size of droplets can affect the surface area of oil droplets which are subjected to the aqueous phase (McClements & Decker, 2000). Since small droplets have a larger contact area between transition metal ions and unsaturated lipids, it is possible that they are oxidized faster. In addition, a larger interfacial area can enhance the accessibility of dissolved oxygen in the aqueous phase to the oil phase (Berton-Carabin et al., 2014). Xiao and Huang (2015) reported that emulsions stabilized by kafirin nanoparticles showed lower peroxide values and thiobarbituric acid reactive substances than those emulsions stabilized by polysorbate 80 during 15 days of storage at room temperature. This is because of the larger droplet size in the emulsion stabilized by kafirin nanoparticles. Also, Nasrabadi, Goli, Doost, Dewettinck, and Van der Meeren (2019) reported that flaxseed O/W emulsion stabilized by flaxseed protein and mucilage showed lower peroxide values and thiobarbituric acid reactive substances compared to flaxseed O/W emulsion stabilized by polysorbate 80 during 28 days of storage at 50 °C. Also, they stated that in addition to the provision of a thicker interfacial layer by flaxseed protein and mucilage complex, as compared to the polysorbate 80, a lower oxidation rate of the emulsion stabilized by flaxseed protein and mucilage could be explained by larger droplet size.

On the other hand, some studies have shown a decrease in oxidation rate by decreasing the droplet size (Gohtani, SirendiYamamoto, Kajikawa, & Yamano, 1999; Ries, Ye, Haisman, & Singh, 2010). This decrease in oxidation rate could be attributed to factors such as variations in the interfacial properties that stem from the droplet curvature on its surface and from large droplets. These ultimately result in alterations to the packing properties of solid particles. Therefore, as oxidation begins in a droplet, it can propagate through an emulsion containing fewer larger droplets, though with a higher speed compared to one containing smaller droplets (Villeneuve, Durand, & Decker, 2018).

2.1.3. pH

The pH of the emulsions stabilized by solid particles based on proteins can have an impact on lipid oxidation rate by altering the charge of proteins. In addition, the pH of the aqueous phase can influence the solubility of iron in the aqueous phase (McClements & Decker, 2000). Mancuso et al. (1999) suggested that the water solubility of transition metal ions decreases at high pH values and that they may precipitate onto the surfaces of oil droplets which results in accelerating the lipid oxidation rate. Also, emulsions stabilized by zein/pectin complex particles exhibited lower amounts of lipid hydroperoxides and malondialdehyde at pH 3.0 and 3.8, compared to pH 5.0 during 21 days of storage at 50 °C. In fact, at a lower pH, zein/pectin complex particles occurred in association with more favorable intermolecular interactions and as an interfacial structure in the bulk phase, resulting in better viscoelasticity and stability (Zhou et al., 2018a).

Other factors which can influence the lipid oxidation in O/W emulsions include chemical structure of lipids, oxygen concentration, and interactions with aqueous phase components which have been explained in previous reviews (Berton-Carabin et al., 2014; McClements & Decker, 2000).

3. The most food-grade solid particles used for stabilizing Pickering emulsions

Food grade solid particles (biological origin) are gradually replacing inorganic particles for producing Pickering emulsions with food-grade status. It is remarkable that an essential, technological challenge continues to exist using edible colloid particles, especially protein particles when formulating Pickering emulsions. Polysaccharides, proteins, polyphenols, lipids, and bacterial particles have been widely applied to stabilize Pickering emulsions and to have long-term stability (Rayner, Marku, Eriksson, Sjöö, Dejmek, & Wahlgren, 2014). The availability, biodegradability, and nontoxic characteristics of food grade solid particles enable them to be potential substitutes of conventional emulsifiers when aiming to fabricate eco-friendly Pickering emulsions (Zhu et al., 2020).

3.1. Polysaccharides

Polysaccharides are sustainable, accessible, and cheap sources of particulate emulsifiers. They are used in Pickering emulsion stabilization. Polysaccharides can inhibit lipid oxidation of emulsions according to their ability to promote thickening, gelation, stabilization, and, ultimately, increase continuous phase viscosity. This usually leads to a lowered level of diffusion rate for oxygen and pro-oxidant compounds. Increasing the concentration of food-grade polysaccharide particles reduces the lipid oxidation rate due to the formation of a thicker interfacial layer around the oil droplets and forms a thicker interfacial physical barrier. These dense interfacial films around oil droplets can hinder the access of free-radicals chain reaction, pro-oxidants, and oxygen (Kargar et al., 2012; Song, Zheng, Ma, Kang, & Ren, 2020; Xiao and Huang, 2015). Polysaccharides as solid particles in Pickering emulsions are presented in Table 1. In the following, we discuss the role of some important polysaccharides in improving the oxidative stability of Pickering emulsions.

3.1.1. Chitosan

Chitosan, a natural linear polyaminosaccharide, is the second most abundant natural biopolymer after cellulose (Hosseini et al., 2019). The properties of this heterogeneous polysaccharide usually depend on its structure and composition. Viscosity is the most important surface property of chitosan and is based on its molecular size, concentration, pH, cationic character, and ionic strength of the solvent (Chaudhary, Kumar, Kumar, & Sharma, 2020). In recent research, chitosan has been mostly used in Pickering emulsions (Zhou, Zeng, Yin, Tang, Yuan, & Yang, 2018c; Huang, Zhou, Yang, Yin, Tang, & Yang, 2019; Hosseini et al., 2019; Li et al., 2019; Liu, Pei, Peltonen, & Heinonen, 2020; Li et al., 2020; Atarian et al., 2019; Zeng et al., 2017). It is used as a novel Pickering emulsifier with good properties in being bio-sourced, biocompatible, relatively inexpensive and even edible, but due to its high hydrophilic properties, chitosan is not a good surfactant for formulating the O/W emulsions and it requires surface modifications for improving its surfactant properties (Atarian et al., 2019). Myristic and stearic acids are used for modifying chitosan structures in Pickering emulsions. In one research, chitosan-myristic acid showed positive charges of the Pickering emulsion droplets, and prevented lipid oxidation to compare with coating the oil with Tween 80. All amine groups of the modified chitosan were not attached to the carboxylic acid groups of myristic or stearic acids, and some amine groups were free (Hosseini et al.,2019; Atarian et al., 2019). As a result, the charge of emulsion droplets can influence the absorption and removal of transition metal ions which participate in the lipid oxidation process. Nanogels of chitosan in hydrochloride-carboxymethyl starch were used as constituents of stabilized Pickering emulsions, thereby delaying the lipid oxidation rate in view of the fact that they could act as a physical barrier against the closest contact between lipid hydroperoxides and pro-oxidants. Also, both chitosan and chitosan derivatives exhibited antioxidant activities (Li et al., 2020).

3.1.2. Starch

An abundant biopolymer that is used as a solid particle, starch can contribute to the preparation of Pickering emulsions. Starch particles are natively hydrophilic, thanks to their hydroxyl groups (OH), which makes them readily dispersible in water. Starch hydrophobicity against the oil surface depends on the degree of modification, botanical origin,

and size of the starch particles (Hadi, Marefati, Matos, Wiege, & Rayner, 2020).

Different starch modification methods have been applied for the purpose of increasing the stability of Pickering emulsions. These methods include acid hydrolysis, nanoprecipitation, enzymolysis and recrystallization methods. They can increase the hydrophobicity of starch particles. Also, alkaline treatment of starch can be done by reducing the particle size, thereby improving stability (Chen, Ao, Ge, & Shen, 2020).

By providing a layer of adsorbed particles around each oil droplet, starch particles can hinder the access of free-radical chain reactions, thereby inhibiting the lipid oxidation of O/W emulsions (Song et al., 2020). Different types of starch have been evaluated, showing that un-absorbed particles and excess surfactants in the continuous phase could increase the viscosity of a given emulsion and reduce the diffusion of pro-oxidants. This enhances the physical and oxidative stability of Pickering emulsions (Li et al., 2020; Kargar et al., 2012). Starch particles have great compatibility with anionic surfactants and have the ability to reduce the oxidation rate of Pickering emulsions and improve oxidative stability of Pickering emulsions.

Cyclodextrins are produced from starch by enzymatic conversion (cyclodextrin glycosyltransferase along with α-amylase). β-cyclodextrin is an emulsifier that is used for preparing Pickering emulsions. It is a hydrophobic solid particle in the cavity, but is hydrophilic on the external cavity. β-cyclodextrin is understood to form a physical barrier primarily by adsorption at both immiscible interfaces to inhibit adjacent droplets from polymerizing with each other to stabilize the emulsion. β-cyclodextrin acts as an antioxidant, drug carrier and an emulsion stabilizer. On the other hand, the low surface activity of β-cyclodextrin limits its application in food emulsions (Niu et al., 2019).

3.1.3. Pectin

Pectins are hydrocolloids that can be used as thickening agents as well as emulsifying agents. Some pectins such as sugar beet pectins are known to have exceptional emulsification properties because of high contents of protein moiety and acetyl groups. (Liang & Luo, 2020).

Some pectins and their derivatives exhibit antioxidant activity and inhibit lipid oxidation by iron binding capacity and radical scavenging activity. Pectins can be used as a solid particle. They provide protection against the lipid oxidation of Pickering emulsions and interact directly with oxidants and free-radical chain reactions (Zhou et al., 2018a; Jiang et al., 2020).

3.1.4. Cellulose

Cellulose is the most abundant biopolymer on Earth and can be used as an emulsifier. Different types of cellulose have been used as solid particles and showed good oxidative stability (Angkuratipakorn, Sriprai, Tantrawong, Chaiyasit, & Singkhonrat, 2017; Zhang et al., 2019; Kargar et al., 2012). Microfibril cellulose, cellulose nanofibrils, microcrystalline cellulose, and cellulose nanocrystals are excellent candidates that can contribute to the making of Pickering emulsions that are often made according to the acid hydrolysis method (Chen et al., 2020). Their ability is attributed to their high aspect ratio, amphiphilic property, and the ability to self-assemble at oil–water interface (Jiménez Saelices, & Capron, 2018). Cellulose nanocrystals are a famous type of Pickering emulsifiers. Previously, it was claimed that cellulose nanocrystals can stabilize emulsions before the reduction of its surface charge (Low, Siva, Ho, Chan, & Tey, 2020). Cellulose nanocrystal inhibited and retarded the production of hydroperoxides in the unsaturated fatty acids of rice bran oil phase, due to its high crystalline ability, strong intermolecular and intramolecular hydrogen bonds of cellulose nanocrystal structures, and a dense cellulose chain-packing (Angkuratipakorn et al., 2017). Interestingly, the rigid cellulose nanocrystals can be synergistic with non-ionic surfactants at the oil–water interface, by lowering the permeation of oxygen molecules that can inhibit deterioration of the double bonds in the oil structure. By increasing the zeta potential,

microcrystalline cellulose particles were found to be more effective in scavenging and chelating pro-oxidants than modified starch particles. An explanation of this result is that due to the larger size of microcrystalline cellulose particles, as compared to modified starch particles, they form thicker interfacial layers around the oil droplets. This can improve the oxidative stability of microcrystalline cellulose emulsions that are stabilized. However, particles in general have a better lipid oxidation rate than small molecular weight emulsifiers (Kargar et al., 2012).

3.1.5. Other polysaccharides

Some polysaccharides such as kefiran contain amino acids side-chains with antioxidant activity such as methionine, cysteine, tryptophan, proline, and histidine (Xiao and Huang, 2015). Quercus suber bark contains several phenolic acids, suberin, and terpenes (Carriço, Pinto, Graça, Gonçalves, Ribeiro, & Marto, 2019). These antioxidants inhibit the propagation of lipid oxidation rate at the interfacial layer. Hawthorn pectin is characterized by strong antioxidant activity and shows antioxidant activity while acting as the shell-material of zein particles (Jiang et al., 2020). Furthermore, the increase in interactions between gliadin and chitosan made a robust antioxidant shell around the oil droplets for protecting the core (Li et al., 2019; Zeng et al., 2017).

3.2. Proteins

Proteins, particularly globular proteins, are widely used as emulsifiers to form O/W emulsions, due to their excellent surface activity and interfacial stabilization. In the emulsification process, adsorbing proteins at newly generated surfaces of droplets usually result in more droplet disruption due to a low interfacial tension, thereby giving an advantage to the stability of the resultant emulsions that are caused through steric and electrostatic interactions (Tang, 2020). The situation of proteins and their respective concentrations are significant factors in emulsion stability. In O/W emulsions, proteins not only adsorb at the interface and modify along with the incubation of emulsions, but also present as non-adsorbed proteins in the aqueous phase without any significant decomposition. Non-adsorbed proteins can delay lipid oxidation rate by quenching aqueous free-radical chain reactions and/or binding of the oxidation initiators, thereby delaying the lipid oxidation rate. Proteins inhibit lipid oxidation by the scavenging free-radical chain reaction, inactivating reactive oxygen species, and chelating pro-oxidative transition metal ions (such as iron and copper). In addition, proteins can alter the food interfacial properties and physically separate reactive species from oil phase (Gumus, Decker, & McClements, 2017). The protein constructions are composed of amino acids with several side chains and functional groups such as the imidazole ring (histidine), the indole group (tryptophan), and the sulfur moiety (cysteine and methionine), which reinstate their amphiphilic character (Jafari et al., 2020). As a result, they affect the oxidative stability by scavenging free-radical chain reactions or sequestering pro-oxidative transition metal ions (Yang & Xiong, 2015). Proteins usually show antioxidant properties, which lead to protection against chemical degradation of labile bioactive compounds (Jafari et al., 2020). Jiang and Xiong (2015) reported that antioxidant activity of proteins and peptides is based on two effects: 1- chemical effect: by acting as antioxidants and 2- physical effect: by physically stabilizing the emulsion oil droplets and by acting as a steric hindrance so as to free radical chain reaction and pro-oxidants in O/W emulsions (adsorbed proteins). Proteins in both the aqueous phase and interface of O/W emulsions are capable of preventing lipid oxidation. In the aqueous phase, proteins can act as antioxidants for having specific iron binding sites such as transferrin, phosvitin, and lactoferrin. They are better antioxidants when the pH value is above pI, thanks to the attraction of cationic transition metals and free radical scavengers. In the interface, proteins act as active emulsifier/surface and they are better emulsifiers when the pH value is below the isoelectric point due to the repulsion of cationic transition metals (Waraho et al., 2011). Proteins, used in Pickering emulsions, are presented in Table 1. Gliadin and

zein are reportedly the most prevalent proteins used in improving the oxidative stability of Pickering emulsions.

3.2.1. Gliadin

Gliadin is an abundant prolamin-type storage protein in wheat (Qiu et al., 2015) with advantages such as easy access and could be a promising material as an edible Pickering emulsion stabilizer. Gliadin terminals are generally more hydrophobic than the repetitive domains, making gliadin amphiphilic and capable of driving the self-assembly behaviors of gliadin to form nano and micro-structures (Zhang et al., 2020). Gliadin has antioxidant activity due to its amino acids in side-chains, half-cysteine, methionine, and tryptophan. Also, gliadin can inhibit the propagation of lipid oxidation by its hybrid particles at the interface and/or in the continuous phase, as this can eventually enable its capacity to scavenge free-radical chain reactions (Zeng et al., 2017).

3.2.2. Zein

Zein is a class of prolamin protein and the main storage protein of corn. Zein is characterized by its content of sharply defined hydrophobic and hydrophilic domains at its surface. It can behave and occur in self-assembly form a wide variety of mesostructures. Zein has a high proportion of polar amino acids (>50%) and, as a result, the surface of zein particles seems quite hydrophobic (Wang, Hu, Yin, Yang, Lai, & Wang, 2015). Zein peptides have specific hydrophobicity and a molecular weight that enable it to act as a free radical scavenger and to inhibit lipid oxidation. Zein hydrolysates, especially alkaline protease hydrolysates, showed the highest DPPH radical scavenging activity, Fe^{2+} chelating activity, and inhibition of lipid peroxidation (Tang & Zhuang, 2014).

3.3. Polyphenols

Polyphenols such as some common food flavonoids (e.g. quercetin in onions, green tea, apples, and berries, curcumin in turmeric, kaempferol 7-neohesperidoside in lychee fruit, rutin in apples, buckwheat, citrus, figs, and black and green tea, and naringin in skin of grapefruit and orange) can act as excellent stabilizers of O/W emulsions through their adsorption as water-insoluble particles to the surface of the oil droplets (Luo et al., 2011). The formation of an antioxidant interface in the presence of phenolic compounds considerably enhanced the oxidative stability of Pickering emulsions. Quercetin and curcumin as natural polyphenols can act as W/O Pickering stabilizers. Results on interfacial shear viscosity revealed that quercetin particles anchored stronger at the interface in comparison with curcumin particles (Jafari et al., 2020). Quercus suber bark particles were applied as a multifunctional solid component and contributed to a stable, effective, and innovative Pickering emulsion with a meaningful synergistic protection against oxidative stress (Carriço et al., 2019).

3.4. Lipids

In emulsion production, one can examine the potential of fabricated lipid particles that act as Pickering-type stabilizers. Lipid particles, used in Pickering emulsions, are presented in Table 1. Applications of lipid particles in the stabilization of Pickering emulsions as nano and colloid particles have been investigated in several studies (Gupta & Rousseau, 2012; Pawlik, Kurukji, Norton, & Spyropoulos, 2016; Milsmann, Oehlke, Schrader, Greiner, & Steffen-Heins, 2018; Schröder, Sprakel, Schroën, & Berton-Carabin, 2017; Zafeiri, Norton, Smith, Norton, & Spyropoulos, 2017; Schröder, Sprakel, Schroën, Spaen, & Berton-Carabin, 2018), indicating the role of surface active lipid particles as stabilizer and a physical barrier in the interfacial layer. Lipid particles can be used alone or in combination with other emulsifiers. Emulsifiers can affect the formation of fat crystals with modified polarity (Pawlik et al., 2016). The adsorption of an emulsifier to the particle interface may also serve to modify its surface properties. The presence of solid lipid nanoparticles in emulsions lead to increased emulsion stability by increasing the

viscosity of the sample, thereby changing the properties of the oil–water interface, and influencing particle adsorption and emulsion structure. In one research, solid lipid nanoparticles were used for stabilizing a model food grade O/W emulsion for at least 12 weeks. Over time, the emulsions slowly destabilized as a result of losing solid lipid nanoparticles from the interface (Gupta & Rousseau, 2012).

Colloidal lipid particles can either stabilize or destabilize the emulsions depending on the particle adsorption rate versus droplet formation rate and surface coverage of droplets. At a high surface coverage, colloidal lipid particles form a dense particle layer that becomes an effective barrier against droplet coalescence, resulting in physically stable emulsions (Schröder, Sprakel, Boerkamp, Schroën, & Berton-Carabin, 2019). High melting point fat crystallized as inhomogeneously distributed intra-droplet clusters that push oxidizable lipids to the oil–water interface. This is where they are more available to the aqueous phase pro-oxidants and, thus, more disposed to oxidation. Stabilized Pickering emulsions with colloidal lipid particles exhibited a similar lipid oxidation rate compared to sodium caseinate-stabilized emulsions, which shows that the colloidal lipid particles are not able to increase the chemical stability of emulsions compared to conventional emulsifiers through the physical barrier effect. The amount of colloidal lipid particles surface coverage of emulsion droplets can have an opposite effect. A low surface coverage due to bridging can have a destabilizing effect and, at an upper surface coverage, droplet coalescence could be prohibited (Zafeiri et al., 2017).

3.5. Bacterial particles

Certain types of microorganisms could serve as emulsifiers. They can stabilize Pickering emulsions. Further research is required to understand the mechanism, as the steric barrier is adsorbed by solid particles at the oil–water interface, whereas more precise descriptions are required to promote further applications to fully utilize this newly interested method (Yang et al., 2017). Negative charges existing on bacterial cell walls improve the biocompatibility and promote the formation of highly stable O/W Pickering emulsions due to the electrostatic interactions with a positive charge on polysaccharides. Thermally-inactivated baker's yeast (*Saccharomyces cerevisiae*) and lactic acid bacteria (*Lactobacillus acidophilus* and *Streptococcus thermophilus*) are often used as stabilizers of O/W Pickering emulsion. Bacterial cells can adhere to the oil–water interface and prevent oil droplet coalescence by Pickering stabilization. For instance, Firoozmand and Rousseau (2016) reported that lactic acid bacteria cells were capable of producing one-phase (gel-like) emulsions at high oil ratio. Wongkongkatep et al. (2012) used bacteria and chitosan networks to stabilize Pickering emulsions. They stated that the strong binding attraction of polycationic chitosan and the negatively charged cell surface of bacteria (*Escherichia coli*) promoted the hydrophobic properties and the stability of O/W Pickering emulsion.

3.6. Protein complexes

3.6.1. Protein-polysaccharide complex

Both proteins and polysaccharides are usually used together in the food industry, especially for improving Pickering emulsions stability (Table 1). Polysaccharides interact with proteins and modify oxidation properties of emulsions by thickening, gelling, emulsifying, and steric layer bulkiness (Loi, Eyres, & Birch, 2019). The complexation of antioxidative proteins or peptides with polysaccharides (carbodiimide Maillard-type linkage with or without additional crosslinking by transglutaminase) can be used in physically and oxidatively stable emulsions. Reactions of proper polysaccharides, along with a variety of proteins as heterogeneous polymers, for example, deamidated wheat protein (Wong, Day, & Augustin, 2011), soy protein (Qi, Liao, Yin, Zhu, & Yang, 2010) buckwheat protein (Guo & Xiong, 2013), and rice protein (Li et al., 2013) have generated excellent stabilization capabilities in O/W emulsions. Table 1 shows the protein-polysaccharide complexes that can

be used for oxidative stability of emulsions.

A gliadin/chitosan complex was used for the formation of O/W Pickering emulsions. With this complex, more particles effectively adsorbed and attached at the oil–water interface as an emulsifier to inhibit oil droplets from contacting pro-oxidants in the aqueous continuous phase. Moreover, the improved interactions between gliadin and chitosan made a robust antioxidant shell around the oil droplets to protect the core. Therefore, the gliadin and chitosan complex can prevent oil droplet oxidation (Li et al., 2019; Zhou et al., 2018c; Zeng et al., 2017).

The zein/pectin complex reduced oxidation in Pickering emulsions. Pectin attracts the zein particles at the interface. More zein particles adsorbed on the interface caused a denser and compact interfacial layer, which contributes to isolating oil droplets from the continuous phase in O/W emulsion (Zhou et al., 2018a; Jiang et al., 2020).

Soy protein isolate nanoparticles can be used for modifying the hydrophobicity of surface and emulsifying capacity of cellulose nanofibrils (Zhang et al., 2019). Therefore, soy protein isolate nanoparticles provided a 'green' way to increase the hydrophobicity of cellulose nanofibrils and aided their stability on oil–water interface. This complex made a physical layer on the oil–water interface, which provided the protection to the oil phase to bar it from contact with oxygen.

3.6.2. Protein-polyphenol complex

Pickering emulsions that are stabilized by protein–polyphenol can simultaneously deliver nutrients associated with health benefits (disease-preventing and metabolism-enhancing). In addition, the interactions between proteins and polyphenols can increase the stability of protein based colloid systems and protein stabilized emulsions. Some changes in functional properties of proteins arise from their interaction with polyphenols and depend on the non-covalent or covalent nature of the interactions in which the covalent interactions are more stable (Pham, Wang, Zisu, & Adhikari, 2019). For example, Pickering emulsion with soy protein isolate-anthocyanins covalent interaction showed unique properties, including extraordinary emulsion stability, increased oxidative stability, and resistance to *in vitro* digestion (Ju et al., 2020).

Protein-polyphenol complexes, used in Pickering emulsions, are presented in Table 1. The binding interaction between proteins and polyphenols aided the interfacial adsorption of the particles to the oil droplets. When proteins were adsorbed at the oil–water interface, it resulted in an interfacial concentration of polyphenols and then enhanced oxidative stability. By replacing the interfacial protein with polyphenol, the stability of the emulsions improved, either by partially replacing the protein or co-adsorbing with it (Atarés, Akhtar, & Murray, 2012). Polyphenols have been investigated as antioxidants alongside proteins to prevent oxidation (Zhou, Yan, Yin, Tang, & Yang, 2018b; Ju et al., 2020; Zhao et al., 2020; Zhou et al., 2019; Atarés et al., 2012; Carriço et al., 2019). Protein-polyphenol complexes exhibited strong antioxidant activities and excellent emulsifying properties, thereby increasing their effectiveness for applications in foodstuffs (Zhou et al., 2018b).

The proline-rich gliadin and proanthocyanidins binding attraction was used for manipulating the self-assembly nucleation process of gliadin and to construct dual-function hybrid particles. This strategy simplified interfacial adsorption and deposition of the gliadin-based particles through the special attraction interaction between gliadin and proanthocyanidins. Pickering droplets as building units assembled into an interconnected three-dimensional network structure, caused viscoelasticity and ultra-stability emulsions. Interfacial membranes were fabricated by solid particles (as antioxidants) and served as a valid barrier against lipid oxidation (Atarés et al., 2012).

A high concentration of zein nanoparticles were adsorbed at the oil–water interface, causing a higher interfacial concentration of gallic acid and then increasing the oxidative stability (Zhao et al., 2020). On the other hand, the gallic acid percentage, which was determined by the interfacial loading content of zein nanoparticles, took an important

effect as a physical barrier on the oxidative stability of zein nanoparticles-stabilized Pickering emulsions. Thus, both zein nanoparticles and gallic acid have effective roles in preventing oxidation.

4. Strategies for improving oxidative stability of Pickering emulsions

4.1. Manipulating the properties of interfacial layer

The properties of the interfacial layer (thickness, permeability, composition, and charge) play an important role in lipid oxidation of emulsions. Therefore, the manipulation of interfacial properties have been a focus so as to further stabilize emulsions against oxidation (Berton-Carabin et al., 2014).

4.1.1. Increasing the thickness of interfacial layer

The interfacial layer can act as a physical barrier that separates transition metal ions in the aqueous phase from unsaturated fatty acids (Silvestre, Chatyasit, Brannar, McClements, & Decker, 2000). Thus, it can be helpful to develop solid particles which are able to form thick interfacial layers around oil droplets (Kargar, Spyropoulos, & Norton, 2011). Liu et al. (2019b) showed that the treatment of faba bean protein isolate with microbial transglutaminase reduced the formation of conjugated dienes and hexanal structures compared to the emulsion stabilized with faba bean protein isolate. This increase in oxidative stability might be due to the formation of a thicker interfacial layer as evidenced by an enlarged emulsion particle size (Kargar et al., 2011). Microbial transglutaminase induces cross-linking at the side chains which creates branched polymers and steric constraint. The majority of the peptide segment of the branched polymers may not come into direct contact with the interface. As a result, a thick layer is formed that protrudes from the surface of the oil droplet (Liu & Damodaran, 1999). Also, it has been reported that the interfacial layer produced by chitosan hydrochloride/carboxymethyl starch complex nanogels can act as a physical barrier against the proximity between pro-oxidants and lipid hydroperoxides (Li et al., 2019). In addition, partial gelatinization of starch granules improved barrier properties as well as functional utility and process stability of emulsions stabilized by starch granules (Marefati, Rayner, Timgren, Dejmek, & Sjöö, 2013; Timgren, Rayner, Sjöö, & Dejmek, 2011). Furthermore, partial gelatinization of starch granules in Pickering emulsions stabilized by starch granules was useful for effective encapsulation of sensitive substances such as curcumin (Marefati, Bertrand, Sjöö, Dejmek, & Rayner, 2017) and for the encapsulation of oils rich in omega-3 (Marefati, Sjöö, Timgren, Dejmek, & Rayner, 2015).

Some studies have reported that the combination of proteins and polysaccharides took form via electrostatic interactions, while enhancing the oxidative stability of Pickering emulsions by providing a thick interfacial layer. For instance, Zhou et al. (2018a) constructed HIPE with high oxidative stability by designing an interface architecture via manipulating the interfacial behavior, self-assembly, and packing behavior of zein particles using the interaction between pectin and zein. Also, Zhang et al. (2019) modified forms of oxidized surface cellulose nanofibrils with soy protein isolate. They observed that emulsions stabilized by soy protein isolate/cellulose nanofibril complexes showed remarkably lower peroxide value than emulsions stabilized by pure soy protein isolate after 14 days of storage at 40 °C. Liu et al. (2020) reported that preparing emulsions by adding a secondary layer of chitosan to an existing faba bean protein isolate O/W emulsion led to a thicker and cohesive/compact layer than that of faba bean protein isolate O/W emulsion itself. This thicker layer can prevent the coalescence or flocculation of droplets through steric stabilization which results in improving physical stability. In other words, a better and stable adsorption of protein is achieved at the interfacial layer which can suppress oxidation at the contacting border between the oil phase and pro-oxidants in the aqueous phase. In addition, enhancing the protein surface load and droplet size results in a decrease of the surface area

(Liu, Bhattarai, Mikkonen, & Heinonen, 2019). Also, some studies have been shown that complex solid particles containing combination of gliadin and chitosan (Zeng et al., 2017) and combination of zein and chitosan (Wang et al., 2015) in Pickering emulsions were more effective in reducing lipid oxidation rate, as compared to proteins themselves.

Different methods for the preparation of protein-polysaccharide complexes can influence the thickness and compactness of the interfacial layer. These methods include (1) formation of a protein-polysaccharide complex through electrostatic interaction and then regarding it as an emulsifier and (2) adding the polysaccharide to an existing emulsion emulsified by protein to form a second layer around the oil droplets (Berton-Carabin et al., 2014). Emulsions that had been prepared by the addition of an extra outer layer of chitosan to an existing faba bean protein isolate emulsion via electrostatic attraction were more effective than emulsions prepared by a soluble faba bean protein isolate-chitosan complex and also than emulsions prepared by the addition of an extra outer layer of non-interactive chitosan to an emulsified faba bean protein isolate emulsion. They were more effective in reducing the formation of conjugated dienes and various volatile compounds during 7 days of storage at 37 °C. This result can be explained by a higher thickness/compactness of emulsions that were prepared by the addition of an extra outer layer of chitosan to an existing faba bean protein isolate (Liu et al., 2020).

4.1.2. Applying compounds with antioxidant activity for the fabrication of solid particles

In some studies, applying a combination of protein and polyphenols for the fabrication of solid particles led to an increase in the physical and oxidative stability of Pickering emulsions. For instance, tannic acid can significantly enhance the emulsifying properties of zein nanoparticles. Tannic acid showed significant radical scavenging activity and chelating transition metal ions as a result of *in vitro* assays (Gülçin, Huyut, Elmastaş, & Aboul-Enein, 2010). Therefore, zein-tannic acid solid particles can make a protective shell against oxidation due to the powerful antioxidant activity of tannic acid. Moreover, the existence of a shell that formed from the zein-tannic acid nanoparticles can inhibit close interaction between fatty acids and air in the emulsion (Zhou et al., 2019). Also, Zhou et al. (2018b) observed that the interfacial layer which is constructed by proline-rich gliadin-grape seed proanthocyanidins particles reduced the lipid oxidation rate by acting as a physical barrier against the interaction between pro-oxidants and lipid hydroperoxides, while also blocking the chain reaction of lipid oxidation via free radical scavenging activity of grape seed proanthocyanidins. At a concentration of 50 mg/L, grape seed proanthocyanidins exhibited significant radical scavenging activities against superoxide anion and hydroxyl radicals (Bagchi, Garg, Krohn, Bagchi, Tran, & Stohs, 1997). Furthermore, Ju et al. (2020) reported that Pickering emulsion stabilized by soy protein isolate-anthocyanin complex nanoparticles showed lower lipid hydroperoxide and malondialdehyde content than those stabilized by soy protein isolate alone. Also, the lipid oxidation further decreased with an increased amount of anthocyanin. They stated that soy protein isolate-anthocyanin complex nanoparticles can block the chain reaction of lipid oxidation via radical scavenging activity of anthocyanin (Ju et al., 2020).

4.1.3. Manipulating the charge of interfacial layer

A number of studies have suggested that the lipid oxidation rate in emulsions can be inhibited through manipulating the charge of the interfacial layer. According to Hu et al. (2003b), cationic protein can inhibit lipid oxidation through electrostatic repulsion of transition metal ions away from the lipid droplets (Hu et al., 2003b). Kellerby et al. (2006) stated that the low lipid oxidation rate in O/W emulsion stabilized by β-lactoglobulin at pH values below the pI of the protein could be attributed to the positive charge of the protein at this pH. Hosseini et al. (2019) stated that the lower oxidation rate of emulsions stabilized by chitosan-myristic acid nanogel than emulsions stabilized by Tween 80

can be explained by the positive charge of the oil droplets of the emulsion stabilized by chitosan-myristic acid nanogel.

4.2. Crowding oil droplets at high packing fraction

Crowding the oil droplets at a high packing fraction can generate a viscoelastic system which can inhibit the diffusion and transfer of transition metal ions and other pro-oxidant compounds in the aqueous phase toward the oil–water interface and reduce the lipid oxidation rate. This situation plays an important role in reducing lipid oxidation in Pickering HIPE (Zhou et al., 2018c). Zeng et al. (2017) reported that the most important reason for a lower oxidation rate of Pickering HIPE, stabilized by gliadin-chitosan hybrid particles, is the result of a structure-related phenomenon in this concentrated emulsion due to the crowding droplets at high packing fractions.

4.3. Trapping oil droplets in a gel network

Trapping the oil droplets in a gel network is produced by solid particles and results in inhibiting the diffusion and movement of pro-oxidant compounds to the water–oil interface. Li et al. (2020) stated that the Pickering emulsion stabilized by chitosan hydrochloride/carboxymethyl starch complex nanogels was more effective than those of bulk oil and emulsions stabilized by Tween 80 in reducing lipid hydroperoxides and malondialdehyde contents during 16 days of storage at room temperature. This is the result of trapping the oil droplets in the chitosan hydrochloride-carboxymethyl starch complex nanogel which can be attributed to the fact that the oil droplets were hard to be approached by transition metal ions in the aqueous phase. Also, Hosseini and Rajaei (2020) showed that applying fish oil in the form of Pickering emulsion, when stabilized by chitosan-stearic acid nanogels, reduced the peroxide value and thiobarbituric acid reactive substances of mayonnaise during 15 days of storage at 35 °C.

4.4. Increasing the viscosity of continuous phase

According to some reports, increasing the viscosity of the continuous phase can reduce the lipid oxidation rate of O/W emulsions by reducing the oxygen diffusion rate, oil droplet collision, and mobility of pro-oxidant compounds in the continuous phase (Kargar et al., 2012; Shimada, Okada, Matsuo, & Yoshioka, 1996). For instance, Pernin, Bosc, Soto, Le Roux, and Maillard (2019) investigated the effects of continuous phase viscosity on the oxidation of fish oil in O/W emulsions containing 0.3–0.6% (w/w) guar gum as a neutral polysaccharide without Fe^{2+}-binding ability. They reported that the concentrations of lipid hydroperoxides and aldehydes, along with oxygen consumption in the headspace of the flask containing the emulsion, were significantly lower in the emulsions containing 0.3% or 0.6% (w/w) guar gum than in the control emulsion without guar gum. A complementary experiment was carried out on non-emulsified biphasic systems (i.e. composed of fish oil and the aqueous phase, with or without guar gum). While being contained in closed flasks without a headspace, they showed a partial pressure of oxygen in the oil to remain at 0% throughout storage, whereas it decreased gradually from 21% to 0% in the aqueous phase, with a slower decrease in the presence of guar gum. This confirms limited oxygen transfer from the aqueous phase to the lipid phase in the presence of guar gum, which can be explained by a higher apparent viscosity of the aqueous phase containing guar gum (viscosity multiplied by 118 in the presence of 0.6% guar gum over that of the control, at a shear rate of 12 s^{-1}). In addition, it has been reported that the antioxidative mechanism for xanthan in O/W emulsions can be attributed to its transition metal ions chelating ability and because of its high viscous behavior (Chen, Li, Zhao, Selomulya, Zhu, & Xiong, 2016; Sun, Gunasekaran, & Richards, 2007; Shimada et al., 1996). Kargar et al. (2012) showed that by increasing the concentration of microcrystalline cellulose from 0.5% to 2.5%, the interfacial layer around droplets increased
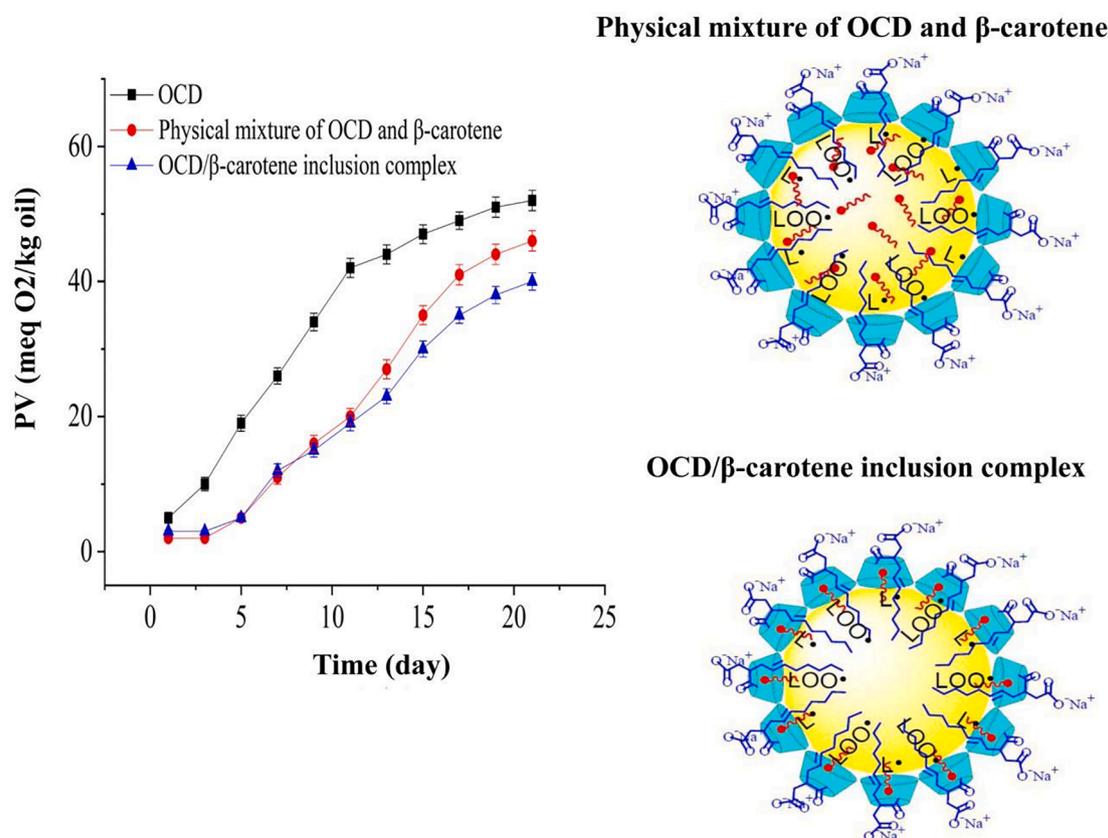
Fig. 5. Peroxide values (PV) of Pickering emulsion stabilized by modified β-cyclodextrin with octenylsuccinic anhydride (OCD), OCD/β-carotene inclusion complex, and physical mixture of OCD and β-carotene (: β-cyclodextrin; : octenylsuccinic anhydride; : oil droplet; : β-carotene). Data extracted from Niu et al. (2019).

in thickness and non-adsorbed microcrystalline cellulose particles also increased in amount within the aqueous phase of the emulsions. This resulted in the formation of the microcrystalline cellulose network in the aqueous phase. These microcrystalline cellulose networks in the aqueous phase can retard lipid oxidation by reducing the mobility of pro-oxidant compounds in the continuous phase. This phenomenon occurs as a result of an increase in the viscosity of the aqueous phase. Also, it has been reported that the cellulose nanofibrils could increase the viscosity of the Pickering emulsion produced by soy protein isolate/ 2,2,6,6-tetramethylpiperidine-nitrogen-oxide which is an oxidized bacterial cellulose. It prevented the movement of transition metal ions in the aqueous phase which resulted in lower peroxide value and thiobarbituric acid reactive substances of this Pickering emulsion, compared with the pure canola oil and Pickering emulsion produced by soy protein isolate after 14 days of storage at 40 °C (Zhang et al., 2019). Moreover, Song et al. (2020) stated that the low peroxide value and *p*-anisidine value of Pickering emulsion stabilized by starch particles during 14 days of storage at 50 °C may be attributed to the presence of unabsorbed starch particles in the aqueous phase, which would enhance the viscosity of the system and inhibit the movement of transition metal ions.

4.5. Incorporation of antioxidants into solid particles

The activity of antioxidants in reducing lipid oxidation partly depends on the nature of the antioxidant, but also on where the antioxidant is located in the emulsion (Villeneuve et al., 2018). Therefore, increasing the antioxidant concentration at the oil–water interface can reduce the lipid oxidation rate in the O/W emulsion. A novel strategy to accumulate antioxidants at the interface is to use Pickering particles which can act both as emulsion stabilizers and as interfacial reservoirs of antioxidants. Thus, a dual functionality can be achieved in which the solid particles serve as a Pickering emulsion stabilizer and as an interface-anchored reservoir of antioxidants. Schröder et al. (2020) entrapped α-tocopherol and carnosic acid into colloidal lipid particles. They observed that over the 14 days of storage at 25 °C, the accumulation of both conjugated dienes and aldehydes was mostly lower in the Pickering emulsions containing α-tocopherol or carnosic acid in colloidal lipid particles, compared to the control Pickering emulsions containing these antioxidants in the oil droplets. Also, it has been reported that preparing Pickering emulsions by a physical mixture of modified β-cyclodextrin with succinic anhydride and β-carotene showed higher peroxide value than those emulsions prepared by a modified β-cyclodextrin-β-carotene inclusion complex during 25 days of storage at 37 °C (Fig. 5). This may be due to the localization of β-carotene at the interfacial layer via the inclusion complex (Niu et al., 2019). Furthermore, Hosseini et al. (2019) observed that the addition of clove essential oil inside the shell of the nanogels produced by solid particles can be a more useful strategy to reduce lipid oxidation in Pickering emulsions rather than to add clove essential oil inside the core of oil droplets.

5. Conclusion and future trends

Food-grade solid particles based on polysaccharides, proteins, polyphenols, protein-polysaccharide complex, protein–polyphenol complex,

Table 2
The roles of solid particles on Pickering emulsion oxidation.

Solid particle	Pickering emulsion oxidation
Protein	Improving oxidative stability by both physical (increasing interfacial layer thickness) and chemical effects (scavenging free-radical chain reactions, inactivating reactive oxygen species, and chelating pro-oxidative transition metal ions)
Polysaccharide	Improving oxidative stability by forming a gel network, increasing the thickness of interfacial layer, and increasing the continuous phase viscosity.
Colloidal lipid	Unable to improve oxidative stability
Protein-polysaccharide complex	Better antioxidant activity of protein-polysaccharide complex than protein alone due to thicker interfacial layer of protein-polysaccharide complex
Protein-polyphenol complex	Better performance of protein–polyphenol complex than protein alone due to radical scavenging activity and chelating transition metal ions of polyphenols as well as thicker interfacial layer of protein-polysaccharide complex

lipids, and bacteria with proper fabrication or modification can stabilize Pickering emulsions. These food-grade solid particles can enhance the oxidative stability of Pickering emulsions by influencing the interfacial layer properties, namely, thickness, permeability, chemical composition, and electrical charge. Also, some of these solid particles can enhance the viscosity of the aqueous phase and reduce the mobility of transition metal ions. In addition, some of these solid particles can form a gel network and trap the oil droplets inside the produced gel network which results in limiting the diffusion and movement of pro-oxidants (Table 2). Besides, the oxidative stability of Pickering emulsions can be enhanced by the incorporation of antioxidants into the solid particles, thereby positioning antioxidants at the interfacial layer. Further research could be conducted to investigate the effect of food-grade solid particles on antioxidant activity, partitioning, and critical hydrophobicity of antioxidants and on their lipophilized homologues in Pickering emulsions. Also, the nature of interactions between antioxidants and these solid particles is poorly understood at present and further works are required on this matter.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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