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Maillard reaction products as functional components in oil-in-water emulsions: A review highlighting interfacial and antioxidant properties

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ABSTRACT

Background: Lipid oxidation gives rise to the formation of off-flavors and is therefore a major concern for food quality. When present in food emulsions (e.g., milk, yogurts, salad dressings), labile polyunsaturated lipids usually oxidize faster than in bulk oil, which can be mitigated by antioxidants. However, the use of synthetic antioxidants is not desired from a "clean-label" point of view. Therefore, we focus on the potential of Maillard reaction products (MRPs), which are biobased molecules that are formed during heating, and of which some may possess excellent antioxidant and emulsifying properties.

Scope and approach: The *in situ* antioxidant activity of MRPs in emulsion systems is reviewed; effects occurring in the continuous phase and at the interface of oil-in-water (O/W) emulsions are distinguished. A dedicated section of the review focuses on the MRPs that are intrinsically present in various foods.

Key findings and conclusions: MRPs may partition between the continuous phase and the oil-water interface in emulsions, which allows them to counteract lipid oxidation by various physicochemical mechanisms, including metal chelation and free radical scavenging. MRPs intrinsically present in foods are promising components to achieve food products with high oxidative stability, while complying with consumer points of view.

1. Introduction

Oxidative deterioration of lipids is a major concern since it gives rise to undesirable changes in flavor, taste, and appearance of foods, which shorten the shelf life of food products (Chaiyasit, Elias, McClements, & Decker, 2007; Sun, Wang, Chen, & Li, 2011). In addition, it generates compounds with questionable metabolic effect (e.g., hydroperoxides and reactive aldehydes) (Schaich, 2020b), which might damage the nutritional quality of foods, thus making the application of healthy polyunsaturated fatty acids (PUFA) in foods a challenge (Genot, Kabri, & Meynier, 2013; Jacobsen, Let, Nielsen, & Meyer, 2008). Probing the mechanisms of lipid oxidation and antioxidation in multiphase foods is especially relevant because lipids commonly exist as dispersions in foods, such as milk, yogurts, infant formula, dips, salad dressing and so on (Decker et al., 2017). These systems consist of lipids dispersed as small droplets in an aqueous phase, called oil-in-water (O/W) emulsions. In such emulsions, lipids normally oxidize faster than in bulk oil due to the large oil-water interfacial area, as well as the emulsification process which may promote oxidation (Genot et al., 2013; Jacobsen, Horn, & Nielsen, 2013).

The use of antioxidants is an effective strategy to counteract lipid oxidation in emulsions. Addition of synthetic antioxidants (such as butylated hydroxytoluene (BHT) and tertiary butylhydroquinone (TBHQ)) to foods is a common practice owing to their high efficiency and low cost. However, the safety of these antioxidants becomes more and more part of public discussions. Some synthetic antioxidants in high dose may exert potential harmful effects (e.g., tumor-promotion) as shown in animal models, and thus low acceptable daily intake (ADI) values have been established by European Food Safety Authority (EFSA) (e.g., 0.25 and 0.7 mg/kg bw/day for BHT and TBHQ, respectively) (EFSA, 2004, 2012). Due to the lack of complete and accurate information on these synthetic preservatives, consumers have been raising doubts about their consumption (Lorenzo et al., 2017). There is a clear drive toward natural and label-friendly alternatives.

A category of components that may comply with sustainability and naturalness trends and can be applied in O/W emulsions are Maillard reaction products (MRPs) that are formed during heating. They have been reported to hold high potential for antioxidant activity and

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emulsifying properties (de Oliveira et al., 2016; Manzocco, Calligaris, Mastrocola, Nicoli, & Lerici, 2000; Nooshkam, Varidi, & Bashash, 2019). From an optimal activity perspective, surface-active antioxidants are particularly relevant, since they would accumulate at the oil-water interface, the location at which lipid oxidation is presumably initiated (McClements & Decker, 2000, 2018). Therefore, in the present review, we report on the potential of these compounds for developing food emulsions with high oxidative and physical stability.

MRPs are formed by the glycation of amino-bearing compounds with reducing sugars. This may alter the protein structure, and thus lead to the exposure of hydrophobic groups of proteins that have affinity for the oil-water interface. Meanwhile, hydrophilic sugar moieties can extend into the continuous water phase and act as a physical barrier ideally preventing droplet aggregation (Liu, Zhao, Liu, & Zhao, 2011; O'Mahony, Drapala, Mulcahy, & Mulvihill, 2018; Zhang, Li, et al., 2019). Furthermore, MRPs are capable of binding metal ions and scavenging free radicals, and can thereby improve the oxidative stability of emulsions (Nooshkam et al., 2019). In emulsions, if MRPs are used as emulsifiers, they would most likely partition between the interface and the continuous phase, which are both environments where the presence and activity of antioxidant molecules are of high importance (Berton-Carabin, Ropers, & Genot, 2014; Faraji, McClements, & Decker, 2004; Genot et al., 2013). All these features make MRPs promising components for use in food emulsions, although it is good to point out that in literature the various effects as they would occur in different physical locations in food products have not been segmented (mostly an overall effect is reported).

MRPs are inherently present in certain foods (such as coffee, beer, and bakery products) but can also be specifically targeted, using proteins and polysaccharides as starting materials. Great efforts have been made to study the antioxidant activity of these components that is after isolation using specific assays. For more information, we refer through to the following reviews (Hidalgo & Zamora, 2017; Lee & Shibamoto, 2002; Manzocco et al., 2000; Namiki, 1988; Nooshkam et al., 2019). Yet, the antioxidant activity (e.g., radical scavenging and metal chelating activity) of MRPs when measured using indirect methods in the absence of an oxidizable substrate does not necessarily reflect the mechanisms involved when it pertains to lipid oxidation in food systems (Echavarría, Pagán, & Ibarz, 2012), as is the case for many antioxidants (Laguerre, Lecomte, & Villeneuve, 2007). It is therefore extremely important to investigate antioxidant effects of MRPs in systems that do justice to the complexity of the food matrix, which has only very recently become part of the research in this field.

In the present paper, we review the interfacial properties as well as the mechanisms of antioxidant activity of MRPs in O/W emulsions. We start by defining the playing field (emulsions, lipid oxidation, and MRPs). Next, we focus on the properties of the MRPs, both from a physical (emulsifying properties) and chemical (antioxidant activity) point of view. In the next section, we connect this to effects reported for food emulsions stabilized by MRPs. We wrap up with a brief outlook on the future application of MRPs in foods to achieve products that are intrinsically more stable both from physical and oxidative points of view.

2. Emulsions, oxidation, and MR products

2.1. Food emulsions

Emulsions are multiphase systems that consist of at least one polar phase (usually water) and one nonpolar phase (usually oil), with one phase being dispersed as droplets in the other phase. The emulsions we consider in this review are oil-in-water (O/W) emulsions, thus containing small oil droplets dispersed in a water phase. Emulsions are thermodynamically unstable systems that tend to minimize their interfacial area, and therewith, their free energy (ΔG, J) (Equation (1)).

$$\Delta G = \gamma \Delta A \tag{1}$$

where γ (N/m) is the interfacial tension between the oil and water, and ΔA (m^2) is the difference in interfacial area. To avoid phase separation, surface-active compounds (generally referred to as emulsifiers) are used to lower the interfacial tension and provide electrostatic and/or steric repulsion between droplets. Yet, all emulsions are prone to gravitational separation, flocculation, and coalescence depending on the time scale of observation (McClements, 2015).

2.2. Lipid oxidation in emulsions

Lipid oxidation is generally described as a complex sequence of chemical reactions starting from unsaturated fatty acids and oxygen-active species. It takes place through a free radical chain mechanism for which we refer through to numerous comprehensive reviews (see e.g., Frankel, 1980; Schaich, 2013; Schaich, 2020a); here, we will limit ourselves to a general description of the basic mechanisms. Lipid autoxidation can be divided into three stages: initiation, propagation, and termination (Farmer, Bloomfield, Sundralingam, & Sutton, 1942). In the initiation stage, in the presence of an initiator, unsaturated fatty acids (LH) lose a hydrogen atom at an allylic methylene group whereby alkyl radicals ($L^{\bullet}$) are formed. These highly reactive alkyl radicals ($L^{\bullet}$) can quickly react with triplet oxygen to form lipid peroxyl radicals ($LOO^{\bullet}$). Since these radicals have higher energy than alkyl radicals ($L^{\bullet}$), they can abstract hydrogen atoms from another unsaturated fatty acid (LH) to produce hydroperoxides (LOOH) and new alkyl radicals (see also Fig. 2). Hydroperoxides are primary oxidation products that can be quantified using various methods (Gheysen et al., 2019; Merkx, Hong, Ermacora, & Van Duynhoven, 2018; Uluata, Durmaz, Julian McClements, & Decker, 2021). Hydroperoxides can decompose via different pathways (e.g., cyclization, rearrangement, hydrogen abstraction, scission and condensation) to form secondary oxidation products (such as aldehydes, alcohols, hydrocarbons, ketones and volatile organic acids). These products may be quantified by different analyses, such as the ρ-anisidine value (pAV, quantifying total aldehydes), thiobarbituric acid-reactive substances (TBARS, quantifying various compounds including malondialdehyde) (Viau, Genot, Ribourg, & Meynier, 2016), and volatile compounds (e.g., propanal and hexanal) (Jacobsen, García-Moreno, Yesiltas, & Sørensen, 2021). In the termination stage, two radicals react with each other to form stable non-radical compounds, which will terminate the radical chain reaction. In addition to this classic scheme, "hydroperoxide initiation" has been proposed recently: decomposition of (pre-existing) traces of hydroperoxides at the oil-water interface has been hypothesized as a crucial reaction for the initiation of lipid radicals (Laguerre, Tenon, Bily, & Birtić, 2020).

O/W emulsions comprise three main regions: the interior of the oil droplets, the continuous water phase, and the interface between these two phases. Molecules will partition between these three regions based on polarity and surface activity. Hydrophobic substances (e.g., tocopherols, oil-soluble pigments) are predominantly located in the oil phase, hydrophilic substances (e.g., salts and metal ions) in the continuous water phase, and amphiphilic compounds (e.g., emulsifiers) at the interface (McClements & Decker, 2000). The location of these substances will largely impact lipid oxidation, (systematically reviewed by Berton-Carabin et al., 2014), since lipid oxidation initiation in emulsions is considered to take place at the oil-water interface where pro-oxidants (e.g. transition metals and oxygen) and unsaturated fatty acids (or trace hydroperoxides) come into contact (Berton-Carabin et al., 2014; Laguerre et al., 2020). The large interfacial area could thus promote the initiation of lipid oxidation, although it is good to keep in mind that the actual course of the reaction is a result of reaction kinetics, in combination with diffusion, and advection effects taking place (McClements & Decker, 2000). For instance, hydroperoxides may diffuse to the interface, which can favor their contact with pro-oxidants thereby

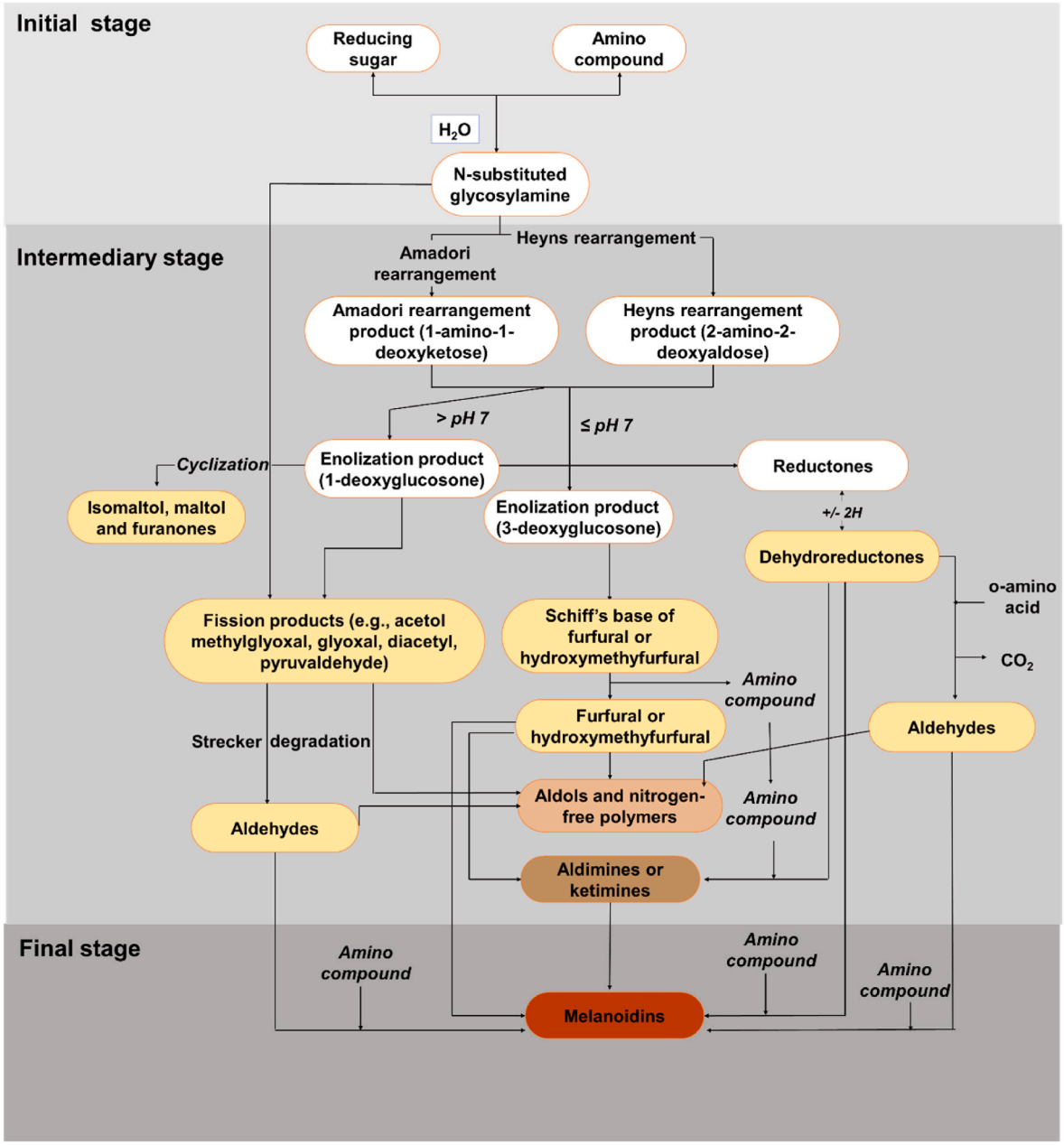

Fig. 1. Schematic representation of the Maillard 'reaction'. Adapted with permission from Hodge (1953). Copyright 2011 American Chemical Society.

accelerating lipid oxidation.

2.3. Maillard reaction

The Maillard reaction (MR) was first detected by Louis Camille Maillard in 1912 (Maillard, 1912) and comprises of a complex series of chemical reactions between carbonyl groups (in reducing sugars) and free amino groups in proteins, peptides, or amino acids that lead to non-enzymatic browning. Only in 1953, the first consolidated scheme of the MR was proposed (Hodge, 1953), which comprises of three stages termed: initial, intermediary, and final (Fig. 1), although in practice these phases can occur simultaneously and are interrelated (Silván, Assar, Srey, Dolores Del Castillo, & Ames, 2011).

In the initial stage, condensation reactions take place between carbonyl groups and free amino groups (mainly ε-amino groups) to form unstable Schiff base compounds (O'Brien & Morrissey, 1989) that undergo cyclization and in turn form reversible *N*-substituted glycosylamines (O'Brien & Morrissey, 1989). *N*-glycosylamines from aldose generate Amadori compounds (1-amino-1-deoxyketoses), whereas those from ketose generate Heyns compounds (2-amino-2--deoxyaldoses) (Davidek & Davidek, 2004). Both components do not lead to brown color, but the nutritional value might be reduced due to the decrease in amino acid availability (de Oliveira et al., 2016).

The intermediary stage starts with the decomposition of Amadori and Heyns compounds via different routes (Hellwig & Henle, 2010). At acidic pH, they undergo 1,2-enolization to generate furfural or hydroxymethylfurfural (HMF), whereas at alkaline pH, they undergo 2, 3-enolization to generate reductones (e.g., 4-hydroxy-5-methyl-2, 3-dihydrofuran-3-one (HMF_{one})) and fission products (e.g., acetol, glyoxal, and methylglyoxal). The dicarbonyl compounds formed can react with amino acids leading to aldehydes and aminoketones via Strecker degradation (Yaylayan, 2003), or react with arginyl and lysyl residues to yield advanced glycation end-products (AGEs), such as N^{ε}-(carboxy-methyl)lysine (CML) and N^{ε}-(carboxyethyl)lysine (CEL)

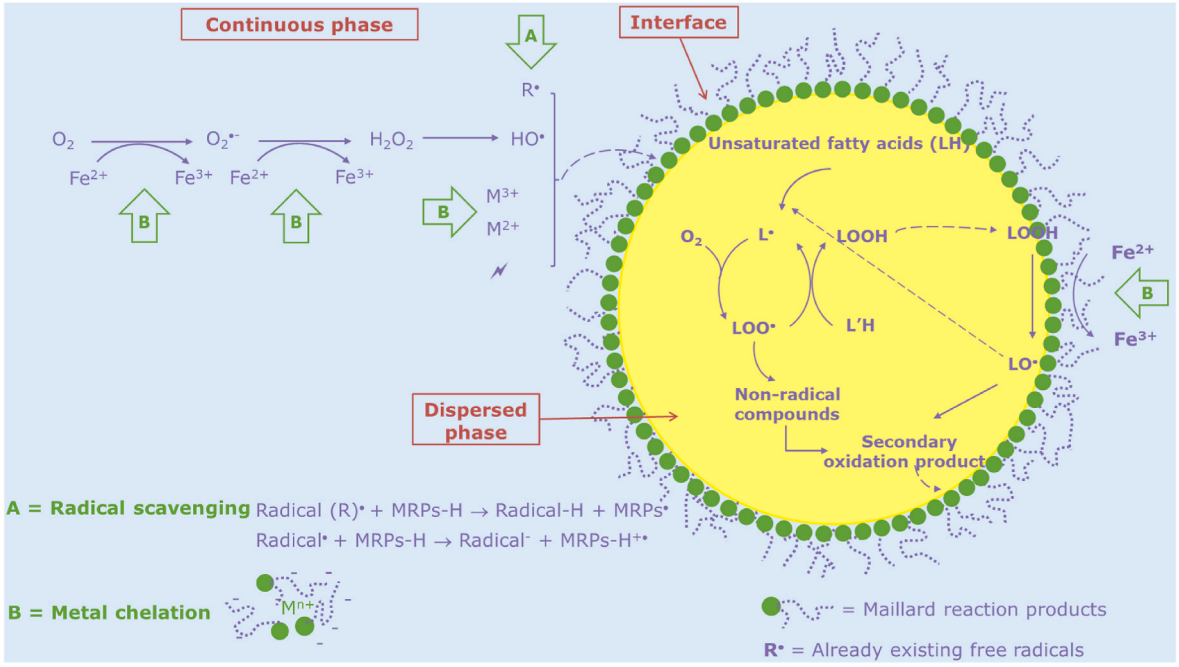

Fig. 2. Antioxidant mechanisms of Maillard reaction products (MRPs) in oil-in-water emulsions.

(Han et al., 2013). In this stage, a yellowish color, flavor formation, and increased reducing power are observed (Nooshkam et al., 2019).

In the final stage, the reactive compounds from the intermediary stage may undergo different reactions (including retro-aldolization, isomerization, rearrangement, and condensation), resulting in the formation of brown-colored, nitrogen-containing and high-molecular-weight polymerized products, called melanoidins (Martins, Jongen, & Boekel, 2001). The chemical structure and formation mechanism of these compounds are still not fully understood. The final phase of MR is mainly responsible for color and flavor formation in most thermally processed foods.

Based on the stage of the MR, MRPs with different features may be created, although it is intrinsically complex to control the reaction. A few studies have tried to limit the MR to the initial stage to preserve emulsification properties of proteins and prevent the formation of advanced glycosylation end-products (dAGEs) of which the intake has controversial physiological consequences (Delgado-Andrade & Fogliano, 2018; Oliver, Melton, & Stanley, 2006; Sedaghat Doost, Nikbakht Nasrabadi, Wu, A'yun, & Van der Meeren, 2019). Other researchers have focused on e.g., antioxidant, antimicrobial, and anti-inflammatory activity, of melanoidins using them as functional food ingredients (Martinez-Gomez, Caballero, & Blanco, 2020; Mesías & Delgado-Andrade, 2017).

2.4. *Emulsifying properties of Maillard reaction products*

The emulsifying properties of some MRPs were first demonstrated by Kato and co-workers (Kato, Murata, & Kobayashi, 1988, 1990). It is generally accepted that both the protein and carbohydrate parts of the MRPs contribute to the reported emulsifying properties (Liu et al., 2011; O'Mahony et al., 2018; Zhang, Li, et al., 2019). The MR results in (partial) protein unfolding, and exposure of hydrophobic groups which increases their affinity for the oil phase. Besides, the hydrophilic carbohydrate moieties extend into the continuous phase, which can prevent droplet aggregation through steric hindrance and/or electrostatic repulsion. Recently, Li and co-workers found that glycation could increase the flexibility of soy protein isolate (i.e., conformational rearrangement of the tertiary protein structure upon external environment changes), thereby facilitating adsorption at the oil-water interface (Li, Cui, et al., 2019; Li, Wang, et al., 2019). Publications related to the physical stability of emulsions with MRPs are summarized in Table S1.

Emulsions stabilized with MRPs have been reported to resist various environmental stresses better than those stabilized with proteins alone. For example, Drapala, Auty, Mulvihill, and Mahony (2016) found that whey protein hydrolysate-maltodextrin MRPs stabilized infant formula emulsions exhibited excellent thermal stability (resistant to bridging flocculation due to the increased steric hindrance of maltodextrin). Emulsions stabilized with MRPs made from soy whey protein isolate and fenugreek gum did not show a significant change in average droplet size after 21 days of storage at 25 °C in the presence of 0.5 M NaCl, or at pH close to the isoelectric point (~pH 4.0) (Kasran, Cui, & Goff, 2013; Kasran et al., 2013). In addition, soy protein isolate-soy soluble polysaccharide MRPs were able to protect citral in emulsions during exposure to simulated gastric and intestinal fluids (Yang et al., 2015).

The emulsifying properties of MRPs are affected by several parameters, such as reaction time, structure and molecular weight of carbohydrates and proteins, protein:carbohydrate ratio, overall net charge, etc. Miralles, Martínez-Rodríguez, Santiago, van de Lagemaat, and Heras (2007) found that the emulsifying capacity of β-lactoglobulin--chitosan MRPs (formed at 40 °C and 79% relative humidity) increased with reaction time up to 2 days, after which the capacity decreased. Likewise, the freeze-thaw stability of emulsions stabilized with soy protein hydrolysate-dextran MRPs increased and then decreased for MRPs prepared at increasing incubation time during their production. This may indicate that early stage MRPs facilitate emulsification, and emulsion stability, and later stage MRPs lose these capacities. Delahaije, Gruppen, Van Nieuwenhuijzen, Giuseppin, and Wierenga (2013) showed that steric stabilization of oil droplets depends greatly on the molecular weight of the carbohydrates attached to patatin, a protein purified from potato, with beneficial effects found for Mw > 500 Da. Similarly, Wong, Day, and Augustin (2011) prepared MRPs from soluble wheat proteins and dextrans D10 or D65 (Mw 6400 Da or 41000 Da, respectively), and found that the larger dextran D65 that is conjugated at the N-terminal domain of the protein leads to interfacial layer around the oil droplets (23.6 nm) thicker than the smaller dextran D10 that conjugates with the C-terminal domain (21.2 nm).

3. Antioxidant activity of the Maillard reaction products

3.1. Standard assays

The antioxidant activity exerted by MRPs is based on a wide variety of mechanisms, including free radical scavenging (e.g., hydroxyl, superoxide, and peroxyl radicals), chelation of metal ions, and breakdown of radical chain reactions (Echavarría et al., 2012; Langner & Rzeski, 2014; Nooshkam et al., 2019; Vhangani & Wyk, 2016). All these effects can be measured using the assays summarized in Table 1 which includes their potential antioxidant mechanisms.

The reducing power and/or ferric-reducing/antioxidant power (FRAP) is used to evaluate the electron donating activity that enables MRPs to convert reactive radicals to a stable form (Hamdani, Wani, Bhat, & Siddiqi, 2018). MRPs have substantial reducing activity, probably because (i) the MR alters the protein structure leading to exposure of certain amino acids (e.g., tryptophan, tyrosine, and methionine) that possess electron donating ability (Hamdani et al., 2018); (ii) Amadori products formed in the initial stages and the hydroxyl and pyrrole groups of MRPs formed in the advanced stage of MR might act as electron donors (Fiore et al., 2012; Pawar, Caggioni, Hartel, & Spicer, 2012; Vhangani & Wyk, 2016), and heterocyclic products that are also then formed could provide reducing activity (Karnjanapratum, Benjakul, & O'Brien, 2017); (iii) reductones are able to donate a hydrogen atom to break the radical chain reaction (Wang, Bao, & Chen, 2013).

The metal chelation ability of MRPs can be attributed to hydroxyl, pyrrole or ketone groups (Gu et al., 2010; Morales, Fernández-Fraguas, & Jiménez-Pérez, 2005), anionic melanoidins binding positively charged metals (Morales et al., 2005), and thiol-derived MRPs binding metals in general (Sproston & Akoh, 2016).

Free radical scavenging activity of MRPs has been extensively studied, using 1,1-diphenyl-2-picrylhydrazyl (DPPH), 2,2′-azinobis (3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS), hydroxyl, peroxyl, and superoxide anion radical scavenging activity. The DPPH and ABTS scavenging activities are predominantly attributed to hydrogen donation by intermediate or final MRPs and electron donation by exposed amino groups (e.g., tryptophan, tyrosine, valine, and phenylalanine) (Khadidja, Asma, Mahmoud, & Meriem, 2017; Liu, Li, Kong, Jia, & Li, 2014; Nasrollahzadeh, Varidi, Koocheki, & Hadizadeh, 2017; Sproston & Akoh, 2016). It is relevant to point out that the DPPH assay is normally carried out with relatively high ethanol or methanol concentrations, which may not be fully representative of the antioxidant activity of MRPs when present in an emulsion. MRPs also interfere with the Fenton reaction owning to their ability to chelate metal ions (Han, Yi, Wang, & Huang, 2017). Other antioxidant activities (including hydroxyl radical scavenging activity, superoxide anion radical scavenging activity, oxygen radical absorbing capacity, and (2, 3-bis(2-methoxy-4-nitro-5-sulpho-phenyl)-2H-tetrazolium-5-carboxanilide) tetrazolium salt reducibility) of MRPs have also been studied and confirmed (Nooshkam et al., 2019).

From the above, we can expect that some MRPs may have the potential to improve the oxidative stability of labile molecules when tested under model conditions. However, the fact that some MRPs are reducing agents could also promote oxidation by the regeneration of Fe^{2+} from Fe^{3+}. For example, melanoidins from barley malt could reduce Fe^{3+} to Fe^{2+} in a Fenton system, resulting in an increase of hydroxyl radicals, and thus induce a pro-oxidant effect. Therefore, whether MRPs can slow down lipid oxidation in food emulsions is a question that still needs to be answered, as we try to do later.

3.2. Maillard reaction products and the oxidative stability of O/W emulsion

The antioxidant activity of a compound in foods is influenced not only by its chemical antioxidative capacities (e.g., metal chelating and free radical scavenging capacity) but also by its physical location and partitioning, interactions with other components, and environmental conditions (Decker, Warner, Richards, & Shahidi, 2005). To properly evaluate this, O/W model emulsions have been used for various MRPs, as listed in Tables 2 and 3.

Partitioning of antioxidants in emulsions is one of the key factors influencing the susceptibility of lipids to oxidation. For instance, negatively charged compounds attract cationic metal ions; when such an attraction occurs at the surface of the oil droplets, this might favor lipid oxidation, whereas binding of metal cations by continuous phase components tends to retard lipid oxidation. For clarity, we first review the effects of MRPs present in the continuous phase (Table 2) and later at the interface (Table 3), and finally bring them together for full emulsion systems (Fig. 2).

3.2.1. MRPs in the continuous phase of emulsions

Unadsorbed compounds (located in the continuous phase) have been shown to affect the oxidation of emulsified lipids, and their contribution may be substantial and even overrule the effect of adsorbed compounds

Table 1
Antioxidant activities of the Maillard reaction products (MRPs).

Antioxidant assay	Principle of method	Possible antioxidant compounds	Mechanisms	Reference
Reducing power	Antioxidants reduce ferric chloride/ferricyanide complexes to ferrous form (Perl's Prussian blue color). Medium: phosphate buffer, pH 6.6.	1. Reductones 2. Hydroxyl and pyrrole groups of advanced MRPs (e.g. melanoidins) 3. Exposed amino acids	1. Hydrogen transfer 2. Reducing activity 3. Electron donation	Gu 2010; Hamdani 2018; Wang 2013
Ferric-reducing/ antioxidant power (FRAP)	Antioxidants can reduce ferric iron to ferrous iron. Medium: acetate buffer, pH 3.6.	1. Heterocyclic products 2. Amadori products and thermolysis compounds 3. Reductones 4. Hydroxyl groups of MRPs	1. Reducing activity 2. Reducing activity 3. Hydrogen transfer 4. Reducing activity (electron donation)	Karnjanapratum 2017; Kim, 2013
DPPH or ABTS radical scavenging activity	Antioxidants can convert $DPPH^{\bullet}$ or $ABTS^{\bullet+}$ to stable molecules. Medium: ethanol or methanol ($DPPH^{\bullet}$) or water ($ABTS^{\bullet+}$).	1. Intermediate or final MRPs 2. Exposed hydrophobic amino acids	1. Hydrogen donation 2. Electron donation	Nasrollahzadeh 2017; Sproston & Akoh, 2016, Khadidja 2017; Liu 2014
Metal chelating activity	Antioxidants can chelate metal ions. Medium: aqueous solution.	1. Hydroxyl, ketone, or pyrrole groups of e.g., Amadori products and melanoidins 2. Thiol groups in MRPs	1. Reducing activity and chelating activity 2. Chelating activity	Gu 2010; Morales 2005; Sproston & Akoh, 2016
Hydroxyl radical scavenging activity	Suppressed malondialdehyde formation by scavenging radicals from Fenton reaction. Medium: aqueous solution.	Hydroxyl groups of the MRPs (e.g., melanoidins)	Chelating activity	Han 2017

*DPPH is 1,1-Diphenyl-2-picrylhydrazyl, ABTS is 2,2′-Azinobis (3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt.

Table 2
Effects of Maillard reaction products (MRPs) in the continuous phase on the oxidative stability of O/W emulsions (MR conditions).

Reference	Highlights	Maillard reaction			Emulsions	
		Starting materials	Reaction conditions	MRP properties	Composition and physical properties	Lipid oxidation
Riisom et al. (1980)	Emulsions with MRPs were slightly more stable to lipid oxidation as compared to control emulsions (with lysine only).	Lysine, dextrose	Wet heating (WH): 50 °C, 15, 4, 8, 17, 24 h		Safflower oil (25%), sodium stearoyl lactylate (1%), distilled monoglycerides (1%) *MRPs (1% level basis lysine) were added after emulsification.	Oxygen absorption rates
Wijewickreme and Kitts (1997)	1. Antioxidant activity (AA) glucose-lysine MRPs > fructose-lysine MRPs. 2. Various *in vitro* methods to evaluate oxidative behavior.	Lysine, glucose or fructose	WH: different reaction time, temperature, initial a_w & pH		Tween 80 (0.2 w/v%), linoleic acid (0.75 w/v%), 0.1 M Potassium phosphate buffer (pH 6.8) *MRPs (0.04 w/v%) were added after emulsification.	Oxygen consumption TBARS
Antony et al. (2000)	1. AA increased with reaction time. 2. AA highest between 10 and 15% MRP.	Lysine, honey (expressed as percent glucose)	WH: reflux condenser, 4, 8, 12, 16, and 20 h	Absorbance (450 nm), pH, reducing sugar (refractometry), volatiles	Tween 20 (1%), linoleic acid (10 v%), 0.1 M potassium phosphate buffer (pH 6.2) *MRPs (1–20 v%) were added after emulsification.	Conjugated dienes (CD)
Romero, Doval, Sturla, and Judis (2005)	Soluble MRP high reduction power, and low DPPH and superoxide scavenging. Conjugate good AA in emulsion system.	Sarcoplasmic protein, malondialdehyde (secondary lipid oxidation product)	WH: 80 °C, 4 h, pH 7.6; sol. fraction	Color, protein carbonyl content, AA: reducing power, DPPH, superoxide radical scavenging, total phenolic content	Linoleic acid (0.570 w/v%), Tween-20 (0.578 w/v%), Phosphate buffer (pH 7.17) *MRPs (0, 1 and 10 w/v%) were added after emulsification.	CD, PV, TBARS
Ruiz-Roca et al. (2008)	Severe heat treatment kept lipid peroxidation intact but decreased free radical scavenging activity.	Lysine, glucose	WH: oven, 150 °C, 15, 30, 60, and 90 min	Weight loss, absorbance (280 and 420 nm), pH, free lysine content, AA: DPPH radical scavenging, copper and iron chelation	Tween 80 (0.2 w/v%), linoleic acid (0.75 w/v%), 0.1 M potassium phosphate buffer (pH 6.8) *MRPs (0.04 w/v%) were added after emulsification.	TBARS
Giroux, Houde, and Britten (2010)	Low amount of MRPs added to dairy beverages reduces oxidation of ω-3 polyunsaturated fatty acids during sterilization.	Milk protein concentrate, sucrose, glucose-fructose (1:1) mixture, glucose-galactose (1:1) mixture	Autoclave: 110 °C, 10 min	Color, redox potential (Pt-ring electrode), hydroxymethylfurfural (HMF)	Milk protein concentrate (3.6 wt%), $FeSO_4$ (0.001 wt %), linseed oil (2 wt%), pH 6.7 *Final concentration protein and lactose, 3.5 and 2.0 wt%. *MRPs (5 v%) were added after emulsification.	Propanal and hexanal
Dong et al. (2011)	MRPs did not dramatically alter the antioxidant activity of casein peptides.	Hydrolyzed sodium caseinate, glucose	WH: 80 °C, 12 h, pH 8	Browning, degree of conjugation, AA: DPPH, metal chelating, bitterness evaluation	Tween 20 (1.0 wt%), fish oil (10 wt%) *MRPs (0.001 w/v%) were added after emulsification. Zeta-potential, droplet size, creaming stability	PV, TBARS
Dong et al. (2012)	The extent of Maillard reaction affects the AA of MRPs (increased and then decreased).	Hydrolyzed beta-lactoglobulin, glucose	WH: 90 °C, up to 18 h, pH 8	Absorbance & fluorescence, size, free amino group content, AA: FRAP, DPPH, metal chelating	Tween 20 (1.0 wt %), menhaden oil (10 wt%) *MRPs (0.001 w/v%) were added after emulsification. Zeta-potential, droplet size, creaming stability	PV, propanal
Jung et al. (2014)	DPPH, ABTS, and reducing power increased significantly with heating time. Effective lipid peroxidation inhibition.	Chitooligomer	WH: 80 °C, 0–240 min	UV absorbance and browning, molecular weight (GPChrom), AA: DPPH and ABTS, reducing power	Linoleic acid emulsion, *MRPs solution (50 v%) were added to emulsions.	TBARS
Shen, Bhail, Sanguansri& Augustin, 2014	MRPs added to the aqueous phase of phospholipid stabilized emulsion increased EPA and DHA stability.	Whey protein isolate (WPI) and Sodium caseinate (7:3), glucose and dried glucose syrup (1:1)	WH: 100 °C, 50 min, pH 7.5		Krill oil (20 wt%) *MRPs (3.0 wt%) or fish gelatin were added to emulsions at pH 8.0.	Fatty acid methyl ester Analysis, propanal
Browdy and Harris (1997)	MRPs suppress hydroperoxide and thiobarbituric acid-reactive substance formation, and lowered oxygen.	Low-lactose sweet whey solutions	WH: 65 °C, 12–48 h, pH 8.0	Fluorescence, browning	Tween 20 (3.3 v%), soybean oil (40 v%), whey solution (10–50 w/v%), cuprous sulfate (10 μM, 3.3 v%), phosphate buffer (pH 8.0)	PV, TBARS, oxygen uptake
Sproston and Akoh (2016)	Prevention of lipid oxidation.	L-cysteine, glucose	Dry heating: 85 °C, 2, 4 6h,		Non-fat dry milk, α-lactalbumin-enriched	PV, pAV

(*continued on next page*)

Table 2 (*continued*)

Reference	Highlights	Maillard reaction			Emulsions	
		Starting materials	Reaction conditions	MRP properties	Composition and physical properties	Lipid oxidation
			77% relative humidity	Browning, HMF, AA: ABTS/H_2O_2/HRP decolorization, metal chelation	WPC, lactose, locust bean gum, carrageenan, lecithin, dimodan monoacylglycerol, structured lipid	
Vhangani and Wyk (2016)	Inhibition of lipid oxidation.	Amino acids (Glycine and lysine), sugars (Fructose and ribose)	WH: 60 or 80 °C, or autoclave: 121 °C, 15, 60 and 120 min	Browning, AA: DPPH & peroxyl radical scavenging	MRPs (0.5 wt%), egg yolk (49.5 wt%), sunflower oil (50 wt%)	PV, TBARS, pAV

AA, antioxidant activity; CD, conjugated dienes; PV, peroxide value; TBARS, thiobarbituric acid-reactive substances; pAV, ρ-anisidine value.

Table 3
Maillard reaction products (MRPs) as emulsifiers on the oxidative stability of O/W emulsions.

Reference	Highlights	Maillard reaction			Emulsions		
		Starting materials	Reaction conditions	MRP properties	Composition	Physical properties	Lipid oxidation
Consoli et al. (2018)	Higher physical stability and lower oxidation than sodium caseinate emulsions	Sodium caseinate, maltodextrin, dried glucose syrup	Wet heating (WH): 75 °C, 3–24 h, pH 7.5	Color, rheology, interfacial tension, SDS-PAGE, size exclusion chromatography (SEC), AA: DPPH radical scavenging, FRAP	MRPs 30 wt%, palm oil 4.5 wt%, resveratrol 0.02 wt %, pH 7.5	DS 0.72–1.03 μm, ZP -54 to −51 mV, rheology microstructure, creaming index	DPPH, FRAP
Cermeño et al. (2019)	MRPs had antioxidant and emulsifying activity	Whey protein concentrate/ hydrolysate, carrageenan	Dry heating (DH): 60 °C, 6–48 h, 79% RH	Molecular mass distribution (GP-HPLC), color, extent of conjugation (TNBS method), AA: oxygen radical absorbance capacity	MRPs 1 w/v%, corn oil 30 wt%, pH 4.0	DSD, coalescence/ flocculation index, microstructure, rheology	TBARS
Wang et al. (2019)	Stable against aggregation during storage and oxidation stability due to antioxidant activity and adsorption of modified protein	Egg white proteins, isomalto-oligo-saccharide	DH: 60 °C, 3 d, 79% RH; sol. fraction: 90 °C, 30 min, pH 6.0–9.0	Surface hydrophobicity, particle size, zeta-potential, grafting degree, AA: DPPH and ABTS	MRPs 1 w/v%, Arowana sunflower oil 10 v %	DSD, ZP -60 to −30 mV, protein content at the interface, microstructure	PV
Zha, Dong, et al. (2019)	High physical and oxidative stability. MRPs prevent hydroperoxide transition metal interaction, rather than scavenge free radicals	Pea protein isolate, gum Arabic	DH: 60 °C, 0, 1, 3 and 5 d, 79% RH, pH 7.0	Color, SDS-PAGE, relative solubility, SEM, free Amadori compounds and melanoidins (UV–Vis), free amino groups	MRP supernatant 0.20 wt%, corn oil 2 wt%, phosphate buffer (10 mM, pH 7.0)	DS (D[4,3] 0.75–20.7 μm), ZP -70 to 10 mV	PV, hexanal
Zha, Yang, et al. (2019)	Maillard-reaction leads to cross-linked PPH-GA MRPs; chemical stability enhanced by increased surface hydrophilicity and steric hindrance	Pea protein hydrolysate, gum Arabic	DH: 60 °C, 0, 0, 1, 3 and 5 d, 79% RH, pH 7.0	Color, SDS-PAGE, FTIR, SEM, SEC-multi angle, light scattering, relative solubility, free Amadori compounds and melanoidins UV–Vis, free amino groups, volatiles (GC-MS)	MRP supernatant, 0.20 wt%, corn oil 2 wt%, phosphate buffer (10 mM, pH 7.0)	DS 0.6–1.3 μm, ZP -70 to 10 mV	PV, hexanal
Shi et al. (2019)	Synergetic effects absorbed and unabsorbed MRPs in lipid oxidation	WPI, dextran	DH: 60 °C, 1–14 d, 79% RH	Grafting degree, AA: DPPH, metal chelating	MRPs 1 w/v%, soybean oil 10 wt%	DS 330–580 nm, ZP -35 to −20 mV, protein adsorption	PV
Wang et al. (2020)	MRPs lead to smaller droplets, better storage and oxidative stability than whey protein	WPI, mulberry fruit poly-saccharide	DH: 60 °C, 0, 48, 72 h, 79% RH	Surface hydrophobicity, intrinsic fluorescence spectroscopy, SDS-PAGE, emulsion foaming capacity/ stability, glycation degree AA: DPPH, oxygen radical absorption	MRPs 1% w/v, fish oil 10%, pH 4.0	DS 300–550 nm, ZP -39 to −20 mV, rheology, protein adsorption	TBARS

DH/WH, dry/wet heating; AA, antioxidant activity; DPPH, 1,1-Diphenyl-2-picrylhydrazyl; FRAP, Ferric-reducing/antioxidant power; PV, peroxide value; TBARS, thiobarbituric acid-reactive substances; DS(D), droplet size (distribution); ZP, zeta-potential; SDS-PAGE, sodium dodecyl sulfate polyacrylamide gel electrophoresis; SEM, scanning electron microscopy; FTIR, Fourier-transform infrared spectroscopy.

(Berton-Carabin et al., 2014). Riisom, Sims, and Fioriti (1980) applied lysine-dextrose MRPs (1% level basis lysine) in safflower O/W emulsions, and they found that these emulsions were only slightly more oxidatively stable (as measured through oxygen uptake) than control emulsions (with lysine only). Similarly, limited effect of lysine-honey MRPs (reacted for 4 and 8 h) was observed when added to linoleic acid model emulsions (at 1% level of addition) (Antony, Han, Rieck, & Dawson, 2000). However, when these MRPs were heated for 12–20 h and added at 5–20%, a strong antioxidant effect was observed. Apparently, the antioxidant effect of MRPs depends on the extent of the reaction. Strong antioxidant effect was also reported for milk protein–carbohydrate MRPs added to krill O/W emulsions, which reduced oxidation of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) and lowered propanal concentrations (Shen, Bhail, Sanguansri, & Augustin, 2014). This was attributed to the antioxidant activity of MRPs, although it is good to mention that the intrinsic antioxidant activity of unreacted compounds was not measured.

The antioxidant effect of MRPs added in the continuous phase of

emulsions is probably related to their ability to act as metal chelators and free radical scavengers. Wijewickreme and Kitts (1997) found that lysine-fructose MRPs could bind copper ions significantly less compared to lysine-glucose MRPs, which was related to high antioxidant activity of the latter, whereas the former showed a pro-oxidant effect in O/W emulsions. Binding of metal ions may decrease their availability for chemical reactions and thus inhibit the decomposition of lipid hydroperoxides (Berton-Carabin et al., 2014). This effect is largely influenced by the pH; for instance, casein peptides-glucose MRPs had lower antioxidant activity at pH 3.0 than at pH 7.0 in Tween 20-stabilized emulsions, which could be due to the positive charge of the MRPs at pH 3.0 which may repel the cationic metal ions (Dong, Wei, Chen, McClements, & Decker, 2011).

Unadsorbed MRPs can scavenge free radicals produced in the continuous phase and/or from oxidizing lipids excreted to the continuous phase. For instance, the DPPH and ABTS radical scavenging activity of MRPs prepared from chito-oligomer increased as their preparation time increased, which led to less lipid oxidation in linoleic acid model emulsions (Jung, Park, Ahn, & Je, 2014), and when reacted at 80 °C for 240 min, MRPs (800 μg/mL) even delayed lipid oxidation more strongly than ascorbic acid (800 μg/mL) in linoleic acid emulsions after storage at 40 °C for 4 days (Jung et al., 2014).

Also, combined effects of radical scavenging and metal binding activities have been reported. Casein peptide-glucose MRPs produced at longer reaction time had increased DPPH radical scavenging activity, whereas their ability to chelate metals decreased, overall resulting in an increase in lipid oxidation (Dong et al., 2011). These combined effects may form an explanation for apparently contradictory results in the literature; i.e., the intrinsic antioxidant ability of MRPs does not always correlate with their propensity to limit lipid oxidation in emulsions. For instance, the antioxidant capacity of lysine-glucose MRPs as measured through TBARS formation in an emulsion increased with reaction time up to 60 min and then leveled off, but no correlation was found with lipid oxidation rate (Ruiz-Roca, Navarro, & Seiquer, 2008). Similarly, MRPs prepared from hydrolyzed β-lactoglobulin and glucose showed increased antioxidant activities as a function of heating time but lipid oxidation was not influenced accordingly (Dong et al., 2012).

There are several other effects that may contribute to the complexity of lipid oxidation in such systems, and that we mention here to make the image complete. First, emulsifiers in the continuous phase may interact with MRPs, therewith altering the conformation of the protein moieties in MRPs (Donnelly, Decker, & McClements, 1998). This may expose amino acids with antioxidant activity, thus retarding lipid oxidation (Feng, Schroën, Fogliano, & Berton-Carabin, 2020). Second, prolonging the heating time of the MRPs could lead to protein aggregation (Zhou, Wu, Zhang, & Wang, 2017), and the large aggregates in the continuous phase of emulsions may lead to bridging or depletion flocculation. Also, a change in physical stability of emulsions (e.g., change in the interfacial area) may affect the oxidation of emulsified lipids. However, most studies did not measure the physical stability (e.g., droplet size) of model emulsions, making it difficult to evaluate the actual effect of MRPs on lipid oxidation. Third, environmental conditions (e.g., solvent, pH, and concentration) can be rather different between emulsions and assays used to investigate antioxidant behavior (e.g., DPPH radical scavenging ability is measured in organic solutions). Fourth, the interfacial composition is generally far from equilibrium and changes during storage (Berton-Carabin et al., 2014), and MRPs in the continuous phase may partly replace or adsorb on top of initially adsorbed emulsifiers. This is shown in studies of Browdy and Harris (1997) and Vhangani and Wyk (2016), who used MRPs and Tween 20 (the former study) or MRPs and egg yolk (the latter study), which stresses the importance of (dynamic) interfacial composition.

3.2.2. MRPs at the interface

Although protein glycation by the MR has been used to improve the physical stability of emulsions for about three decades, the use of such MRPs as interfacial antioxidants started only recently (Table 3). Consoli et al. (2018) found that when MRPs prepared from sodium caseinate and maltodextrin or dried glucose syrup were heated for a longer time (from 0 to 24 h), the MRP solutions displayed greater antioxidant activities (FRAP and DPPH radical scavenging activity), and MRP-stabilized emulsions had higher oxidative stability compared to systems containing the starting protein and carbohydrate mixture. This was attributed to the formation of advanced MRPs with antioxidant properties. Wang et al. (2019) and Wang, Wang, Chen, Fu, and Liu (2020) reported that proteins glycated with carbohydrates enhanced the antioxidant activity in aqueous media (DPPH and ABTS radical scavenging activity, oxygen radical absorption capacity) and in emulsions (peroxide value (PV) or thiobarbituric acid-reactive substances (TBARS)). They claimed that the dense and thick interfacial layers created by the MRPs may protect oil droplets from oxidation through physical effects. In the work of Zha and co-workers, this was linked to the physical barrier effect of MRPs to inhibit the decomposition of hydroperoxides (Zha, Dong, Rao, & Chen, 2019; Zha, Yang, Rao, & Chen, 2019). However, such physical barrier effects are questionable given the size of the reactive species involved in oxidation, and the lack of direct experimental evidence for such an effect. First, the thickness or density of the interfacial layers was not tested in these studies, whereas in general, an oil-water interface formed by biopolymers is porous at the scale of pro-oxidant molecules (Berton-Carabin, Schröder, Schroën, & Laguerre, 2021). Second, the physical effect of the adsorbed glycated proteins was not distinguished from their chemical effects (e.g., metal chelating activity) nor from the effect of the glycated proteins remaining in the continuous phase.

In the work by Cermeño et al. (2019), conjugating carrageenan with whey protein concentrate (WPC) led to an enhanced generation of secondary lipid oxidation products (as measured by TBARS) in emulsions, compared to WPC emulsions. However, it was difficult to assess the involved mechanisms, as some physical destabilization of the emulsions occurred upon incubation (coalescence and flocculation). Additional investigations would be needed to elucidate the relationship between the physical and oxidative stability in emulsions, which is probably multifactorial and therefore difficult to decipher.

The effects of MRPs in O/W emulsions are summarized in Fig. 2. In the initiation stage of lipid oxidation, MRPs and proteins can scavenge radicals, therewith delaying the free radical chain propagation process (Fig. 2, arrow A). MRPs and proteins can bind transition metals therewith preventing them from initiating radical formation and decomposing surface-active hydroperoxides (LOOH) (arrow B). When free radicals and unbound metal ions reach the interface to react with unsaturated fatty acids (LH), adsorbed MRPs can quench free radicals and chelate metal ions. It is important to realize that unadsorbed and adsorbed MRPs may contribute synergistically to the oxidative stability of emulsions.

3.3. Maillard reaction products inherently present in foods

MRPs inherently occur in certain foods (e.g., coffee, cocoa, dairy and bakery products) as a result of processing. Although the antioxidant capacity of model MRPs has been already well studied (section 3.2), research regarding the effects of MRPs derived from such foods is still scarce. Therefore, in this section, we review their antioxidant activity and explore their potential for application in emulsions.

Endogenous formation of MRPs in foods has been reported as an antioxidant source. High temperatures applied during food processing often favor the formation of MRPs, which affects the antioxidant profile of the products. Michalska, Amigo-Benavent, Zielinski, and delCastillo (2008) evaluated the development of MRPs during rye bread baking and their contribution to the overall antioxidant activity of bread. They reported that early MRPs formed in bread did not exhibit antioxidant activity, whereas the advanced MRPs formed in bread crust had strong peroxyl and ABTS radical scavenging activities. Likewise, Anese, Nicoli, Massini, and Lerici (1999) studied the effect of drying temperature on the formation of MRPs in pasta. Results showed that antioxidant

potential was associated with the formation of advanced MRPs, but early stage MRPs seemed to have pro-oxidant properties, which may be due to the formation of some highly reactive radicals in the early stages of the MR and the degradation of natural antioxidants (Calligaris, Manzocco, Anese, & Nicoli, 2004). In addition, Serpen and Gökmen (2009) reported that there was a reasonable correlation between color, total antioxidant capacity and acrylamide levels in potato crisps; they revealed that potato crisps had high antioxidant activity, which was the result of the formation of MRPs during the frying process. Lin, Toto, and Were (2015) incorporated ground roasted coffee in ground top round beef and found that roasted coffee was able to lower lipid oxidation (TBARS) to the same or even greater extent than rosemary (containing phenolic antioxidants). Later, Patrignani, Rinaldi, and Lupano (2016) investigated the *in vivo* antioxidant effect of MRPs in biscuits on rats and concluded that rats fed with higher amounts of MRPs had higher serum antioxidant activity (FRAP, ABTS) and lower oxidation damage (TBARS). These findings suggest that MRPs developed in foods have strong antioxidant activity, and therefore, when extracted may be used as functional ingredients (e.g., antioxidants). For example, fructosyl arginine [N-α-(1-deoxy-D-fructos-1-yl)-L-arginine; Fru-Arg], a low molecular weight MRP that can be isolated from aged garlic extract, exhibits antioxidant activity *in vitro* (Ide, Lau, Ryu, Matsuura, & Itakura, 1999; Ryu, Ide, Matsuura, & Itakura, 2001) through hydrogen peroxide scavenging, at a related activity comparable to ascorbic acid (Ryu et al., 2001). Positive effects were also found in Cu^{2+}-induced LDL (low density lipoprotein) oxidation systems for rat pulmonary artery endothelial cells (lower formation of TBARS and inhibited the release of lactate dehydrogenase), and murine macrophages (inhibited release of peroxides) (Ide et al., 1999). The oxidative cleavage of Fru-Arg in these systems may proceed via metal complexing and reducing properties (O'Brien & Morrissey, 1997).

Melanoidins, the final stage MRPs, have also been studied in relation to their strong antioxidant effect. Studies have mainly focused on melanoidins extracted from real foods, including coffee (Bekedam, Schols, Van Boekel, & Smit, 2006; Borrelli, Visconti, Mennella, Anese, & Fogliano, 2002; Delgado-Andrade & Morales, 2005; Morales & Jiménez-Pérez, 2004; Zhang, Li, et al., 2019; Zhang et al., 2019, 2019), vinegar (Liu et al., 2016; Xu, Tao, & Ao, 2007), cocoa (Quiroz-Reyes & Fogliano, 2018; Summa et al., 2008), and beer (Morales & Jiménez-Pérez, 2004). Depending on the types (composition) of foods and the heating conditions, various types of melanoidins with heterogenetic composition, structure and physiochemical properties can be formed. Melanoidins may be divided into melanoproteins (skeletons primarily made up of proteins) and melanosaccharides (skeletons primarily made up of polysaccharides). Melanoproteins are generally formed through cross-linking of proteins and sugars in protein-rich foods (e.g., bread crust, biscuits, and breakfast cereals), and may appear spongy due to the extremely high-molecular-weight network that is largely water-insoluble; melanosaccharides (e.g., from coffee, cocoa, and beer) are generally developed from amino acids and polysaccharides and are soluble in water (Alves, Xavier, Limoeiro, & Perrone, 2020; Morales, Somoza, & Fogliano, 2012; Rufián-Henares & Pastoriza, 2015; Sharma et al., 2021). In general, melanoidins are negatively charged and brown in color with an absorption peak at 420 nm (Wang, Qian, & Yao, 2011). Since the structures of melanoidins are still largely unknown, their antioxidant mechanisms are unclear but have been suggested to be related to their ability to chelate metals, quench radicals, or act as reducing agents (Echavarría et al., 2012; Mesías & Delgado-Andrade, 2017). The metal chelating ability of melanoidins could be ascribed to their anionic nature, which was shown to allow them to form stable complexes with metals similar to anionic hydrophilic polymers (Gomyo & Horikoshi, 1976). Ćosović, Vojvodić, Bošković, Plavšić, and Lee (2010) reported that nitrogen atoms may be responsible for complexing copper ions, and hydroxyl and ketone groups of pyridone or pyranone serve as chelating agents (Wang et al., 2011). Furthermore, melanoidins can scavenge a variety of radicals, such as ABTS, DPPH, and N,N-dymethyl-*p*-phenylenediamine (DMPD) (Borrelli et al., 2002; Morales & Babbel, 2002). For certain melanoidins from pasta and tomato puree, a linear correlation between radical quenching activity and color was found, whereas more complex relations have been suggested for coffee melanoidins (Manzocco et al., 2000). The actual composition is responsible for the different behaviors, but unfortunately, not well understood. In addition, melanoidins exhibit reducing activity, which may be due to the hydroxyl groups on their heterocyclic regions (Vhangani & Wyk, 2016). Apart from this, for melanoidins from coffee, polyphenols and low molecular weight MRPs non-covalently bound to the melanoidins contribute to overall antioxidative ability (Delgado-Andrade, Rufián-Henares, & Morales, 2005; Delgado-Andrade & Morales, 2005; Morales & Jiménez-Pérez, 2004; Rufián-Henares & Morales, 2007; Tagliazucchi, Verzelloni, & Conte, 2010), and may exceed the activity of the melanoidins themselves (Morales & Jiménez-Pérez, 2004).

Melanoidins may be surface-active and thus adsorb at the air-water interface (and overview is in Table 4). Lusk et al. (1987) isolated a high molecular weight (6–20 kDa) melanoidin fraction from beer that lowered surface tension to 66.0 mN/m (the surface tension at the air-water interface is 72 mN/s). It should be noted that this decrease is somewhat limited compared e.g., proteins (Hinderink, Sagis, Schroën, & Berton-Carabin, 2020), especially considering the fact that the concentration used was 5 times higher than in beer. Later, melanoidins isolated from beer foam liquid were shown to form stable other foams independently of the presence of beer proteins, therewith highlighting a more prominent role than previously recognized (Lusk, Goldstein, & Ryder, 1995).

Melanoidins from coffee foam were also investigated (D'Agostina, Boschin, Bacchini, & Arnoldi, 2004; Piazza, Gigli, & Bulbarello, 2008). The total foaming fraction (TFF) from espresso coffee was separated into a carbohydrate-like and a melanoidin-like fraction, and the foaming properties were studied (Fig. 3). D'Agostina et al. (2004) reported that the melanoidin-like fraction exhibited higher foaming capacity and antioxidant activity than the carbohydrate-like fraction, and Piazza et al. (2008) observed stronger viscoelastic interfacial properties in melanoidin-like fraction than the carbohydrate-like fraction.

The potential of certain food melanoidins to stabilize emulsions has also been described in a few patents. Roasted coffee particles (10–20 wt % dry matter melanoidins proteinous part) have been found to remarkably stabilize emulsions against coalescence, while exhausted roasted coffee particles (aqueous extraction at 110 and 180 °C) showed slightly less good droplet stabilization than roasted coffee, which was ascribed to the loss of surface-active materials (melanoidins) during extraction (Pipe, Gehin-Delval, Mora, Vieira, & Husson, 2014). In another patent, plant-derived starting materials (containing reducing monosaccharides, phenolic compounds, free amino acids, and pectin) were heated, which resulted in a mixture with emulsification properties (Da Fonseca Selgas Martins, van der Hijden, Ihechere, & Vreeker, 2014). It was claimed that the heating conditions employed led to the formation of substantial quantities of melanoidins, as evidenced by browning and absorbance at 405 nm. When using model melanoidins produced with arginine, glutamine, fructose, and glucose, it was found that these components were not that effective as emulsifiers, leading to a wide range of oil droplet sizes (20–60 μm), and a free oil layer on top of the emulsions within 24 h after emulsification, and complete phase separation after 6 months of storage at 5 °C (Da Fonseca Selgas Martins et al., 2014). The low molecular weight and purity of the 'model melanoidins' compared to melanoidins isolated from real foods is expected to have been the cause of the differences observed. To the best of our knowledge, no information regarding lipid oxidation in these emulsion systems is available.

4. Conclusions and perspectives

MRPs can locate both in the continuous phase and at the interface of

Table 4
Literature data on surface-active melanoidins extracted from foods.

Reference	Source	Extraction method	Characterization	Applied in	Characterization of systems	Antioxidant results	Antioxidant mechanism
Lusk et al. (1987)	Beer	Size-exclusion and ion-exchange chromatography of 10–50 kDa proteins.	Isoelectric focusing, protein/carbohydrate concentration, absorption and fluorescence spectra		Dynamic surface tension		
Lusk et al. (1995)	Beer foam liquid	Carbohydrates, melanoidins, and 10, 12, 40 kDa proteins prepared by cation-exchange, anion-exchange, and/or preparative HPLC.	Fourier transform infrared spectroscopy	Model beers	Foam quality, reducing sugars, protein assay including Kjeldahl, dynamic surface tension		
D'Agostina et al., 2004	Brown polymers (foaming fractions) of freshly prepared espresso coffee	Isolation of total foaming fraction (TFF) from espresso coffee, 2-propanol/water extraction to obtain an insoluble and soluble fraction. Soluble fraction further fractionated with solid-phase extraction.	Size exclusion chromatography (SEC), color (Color Dilution Analysis), flavor & taste (sensory evaluation), foamability, foam persistence			Melanoidin-rich fractions showed antioxidant properties. More hydrophobic compounds have higher antioxidant capacity.	Nitrogen-containing moieties or polyphenol residues in polymers not polysaccharides. Some antioxidants in the green seed (chlorogenic acids, phenolics), are destroyed by roasting, but overall AA is preserved due to melanoidin formation.
Piazza et al. (2008)	Foaming fractions from ground dark roasted coffee blend	Isolation of TFF and fractionation in carbohydrate-like, and melanoidin-like components.	Interfacial rheology, viscosity, image analysis				
Pipe et al. (2014)	Particles of roasted or green coffee and mixtures thereof	Grinding coffee beans in liquid nitrogen, aqueous extraction, filtration and drying the solid part.	Particle size	Emulsions	Droplet size, optical microscopy		
Da Fonseca Selgas Martins et al., 2014	Plant-derived material with reducing monosaccharides, phenolics, and pectin	Heating to at least 60 °C for at least 1 min.	Optical absorbance at 405 nm (A_{405})	Emulsions	Visual inspection, optical microscopy		

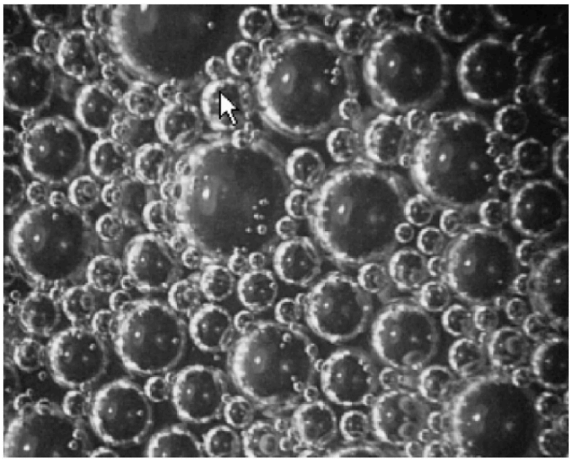

Fig. 3. Stereo-microscope picture (enlargement: 200x) of the foam surface created by stirring non-defatted melanoidin-like foaming fraction under standard conditions. Reprinted from Journal of Food Engineering, 84, Piazza, L., Gigli, J., & Bulbarello, A, Interfacial rheology study of espresso coffee foam structure and properties, 420–429, Copyright (2021), with permission from Elsevier.

O/W emulsions, where they may retard lipid oxidation by various physicochemical mechanisms, including metal chelation and free radical scavenging. Melanoidins isolated from certain food products may have a strong antioxidant effect and have the ability to act as surface-active compounds, so they have a great potential to act as interfacial antioxidants. However, to the best of our knowledge, this has hardly been explored yet.

Although MRPs represent a promising class of interfacial antioxidants with potential use in foods, some challenges remain. First, the compositions and structures of MRPs, especially melanoidins, are not that well known, and the underlying reactions cannot be controlled that easily. Thus, it is difficult to directly link antioxidant effects to molecular or supramolecular structures. There is therefore a great demand for advanced analytical methods that still need to be developed. By identifying the exact compositions and structures, in combination with information on their location in an emulsion, antioxidant efficiency may be predicted. Second, the impact of certain MRPs on human health remains a concern. For instance, acrylamide and its metabolite glycidamide have been shown to be genotoxic and carcinogenic. The Benchmark Dose Lower Confidence Limit ($BMDL_{10}$) was selected as 0.17 and 0.43 mg/kg bw/day for tumors and other effects (EFSA, 2015). Therefore, minimizing the level of harmful compounds through strict control of the MR process is of essence. Third, the feasibility of MRPs in industrial applications needs further evaluation, which includes the design of sustainable preparation processes and evaluation of economic profitability.

Overall, the knowledge gained from this review would allow food scientists to design foods with enhanced oxidative and physical stability by employing MRPs in foods making use of effects taking place at different physical locations (interface or continuous phase).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tifs.2022.02.008.

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