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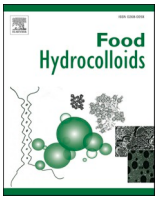

Coffee melanoidins as emulsion stabilizers

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ABSTRACT

The use of conventional food stabilizers (e.g., surfactants and animal-derived proteins) is not in line with consumer demands for natural products. This has led to a great interest in novel emulsion stabilizers. In this paper, we explore the emulsification properties of coffee melanoidins, which are brown polymers made up by polysaccharides, proteins and polyphenols formed during bean roasting. The physical properties and stability of oil-in-water (O/W) emulsions (10 wt% oil) stabilized with 0.25–4 wt% coffee melanoidins were investigated upon storage. Coffee melanoidins can form emulsions with a nearly monomodal size distribution. Upon 28 days of storage at room temperature, emulsions prepared with low (0.25–1 wt%) melanoidin concentrations underwent creaming, flocculation, and coalescence; emulsions prepared with high (4 wt%) melanoidin concentrations gradually transformed from a liquid-like state to a gel-like structure, and emulsions prepared with 2 wt% melanoidins were physically stable.

Stabilization of the emulsions is explained by both interfacial effects and an increased viscosity at high melanoidin concentrations. Surface load determination, confocal laser scanning microscopy (CLSM), and polarized light microscopy revealed that polysaccharide-rich melanoidins were able to adsorb at the droplet surface. We conclude that coffee melanoidins act both as emulsifiers (decreasing the interfacial tension and inducing electrostatic and steric repulsion) and texture modifiers (increasing the viscosity of emulsions). Coffee melanoidins can be used as natural emulsifiers in targeted food products.

1. Introduction

Emulsions are dispersed systems of two or more immiscible liquids, which make up the basic structure of a wide variety of products, such as foods, pharmaceuticals, and cosmetics. Being thermodynamically unstable, they tend to physically destabilize (e.g., gravitational separation, flocculation, and/or coalescence), finally leading to their destruction. Yet, it is possible to produce kinetically stable emulsions, by using texture modifiers or emulsifiers (McClements, 2005). Texture modifiers increase the continuous phase viscosity and thus improve emulsion stability by slowing down droplet creaming or sedimentation, and also coalescence; examples include polysaccharides (e.g., carrageenan, xanthan gum, cellulose) and proteins (e.g., gelatin). Emulsifiers are amphiphilic compounds that can adsorb at the oil-water interface and decrease the interfacial tension; commonly used emulsifiers include surfactants, proteins, and phospholipids (Berton-Carabin & Schroën, 2015; McClements, 2005). Although surfactants and animal-derived proteins are commonly used in food emulsions, from a consumer perspective, this is becoming less and less desired given the current demand for natural and sustainable food ingredients and clean-label foods. This explains the current great interest in identifying new sources of emulsion stabilizers, notably those naturally present in foods.

Coffee is one of the most widely consumed beverages, and contains strong antioxidant compounds (Del Pino-García et al., 2012; Higdon & Frei, 2006). Roasting of coffee beans takes place at high temperatures and low water activity that favors the development of Maillard reaction products (Friedman, 1996), leading to the formation of high molecular weight, brown-colored, nitrogen-containing end-products, known as melanoidins. The major components of coffee melanoidins are polysaccharides (mainly galactomannans and arabinogalactans type II), proteins, and phenolic compounds (Bekedam et al., 2006; Borrelli et al., 2002; D'Agostina et al., 2004; Moreira et al., 2012, 2014; Nunes et al.,

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2012). Some of these compounds (e.g., polysaccharides, proteins, and polyphenols) are expected to have properties that can be instrumental in stabilizing emulsions. For example, galactomannans (from Locust bean gum, guar gum, fenugreek gum, and tara gum) consisting of a β-(1 → 4)-linked D-mannose backbone with α-D-galactose side groups are able to form highly viscous solutions and exhibit some surface activity, leading to physically stable emulsions (bib_garti_and_reichman_1994Garti & Reichman, 1994; Wu et al., 2009). In addition, arabinogalactans are often covalently linked to proteins and thus present as arabinogalactan proteins (AGPs), which are believed to predominantly determine the emulsifying property of the widely used emulsifier gum Arabic (Dickinson, 2003). Based on these insights, it is likely that coffee melanoidins have potential as emulsion stabilizers. This is strengthened by the fact that melanoidins have been found instrumental in stabilizing foams (D'Agostina et al., 2004; Piazza et al., 2008). extracted a total foaming fraction from espresso coffee and separated it into two fractions based on solubility in 2-propanol/water. The soluble fraction exhibited a prevailing protein-like character and had better foamability, whereas the insoluble fraction showed a prevailing polysaccharide-like character that contributed more to the foam stability via the thickening behavior and/or the interaction with absorbed proteins at the air-water interface (D'Agostina et al., 2004; Piazza et al., 2008). The foamability of coffee melanoidins has been related to their amphiphilic nature: furan and pyrrole-like hydrophobic moieties and the negatively-charged hydrophilic moieties (Bekedam et al., 2007), whereas polysaccharides can behave as viscosity improvers to enhance foam stability (Nunes & Coimbra, 1998).

Coffee melanoidins constitute a significant part of the diet of coffee drinkers (Fogliano & Morales, 2011), and they can also be used as food ingredients in the search for healthier and tasty foods. For example, coffee melanoidin-enriched bread was able to elicit satiety and modulate postprandial glycemia and other biomarkers (Walker et al., 2020). Our study aimed to explore the potential of coffee melanoidins as food ingredients to stabilize emulsions. Coffee melanoidins at the concentrations of 0.25–4 wt% were used to stabilize purified rapeseed oil-in-water (O/W) emulsions, and the physical properties of these emulsions were investigated during 28 days of storage. The results showed that these components have great potential for application in emulsions.

2. Materials and methods

2.1. Materials

Dark roasted arabica coffee beans (Illy®, Trieste, Italy) and refined rapeseed oil were purchased from a local supermarket (Wageningen, the Netherlands). The latter was stripped with alumina powder (Alumina N, Super I, EcoChrome™, MP Biomedicals, France) to remove surface-active impurities and tocopherols (Berton, Genot, & Ropers, 2011). Whey protein isolate (WPI, 88.11 wt%, dry basis) was supplied by Davisco (Lancy, Switzerland). D-Glucose, chlorogenic acid, calcofluor white, rhodamine B, BODIPY 505/515, sodium dodecyl sulphate (SDS), hexane, and sulfuric acid (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium carbonate decahydrate and phenol were obtained from VWR (Radnor, PA, USA). Folin-Ciocalteu reagent and ethanol (95%) were purchased from Merck Millipore (Merck, Germany). Dichloromethane was from Actu-All Chemicals B.V. (Oss, The Netherlands). All chemicals and reagents used in this study were of analytical grade. Ultrapure water was obtained with a Millipore Milli-Q water purification system and used throughout the experiments.

2.2. Preparation of high molecular weight coffee melanoidins

High molecular weight coffee melanoidins were extracted from roasted coffee beans according to the procedure described by (Zhang et al., 2019) with some modifications. In brief, dark roasted coffee beans were ground to powder with a particle size <0.45 mm using a Spex sample Prep 6870 cryogenic mill (Minneapolis, Minnesota, US). The powder was then defatted by extraction with dichloromethane (1:3, w/v, three times, room temperature); the solvent was removed by drying the sample in air overnight. After that, 100 g of the defatted powder were extracted with 1.2 L of water at 80 °C for 20 min. The suspension obtained was filtered through a Whatman 595 filter paper (Billerica, MA, US) under vacuum. An aliquot of the filtrate was subjected to ultrafiltration using an Amicon stirred cell (Millipore Co., MA, US) equipped with a 10 kDa nominal molecular weight cut-off regenerated cellulose membrane (Merck, Germany). The obtained retentate was re-filled up to 100 mL with water and the ultrafiltration process was continued to eliminate the low molecular weight components. This washing step was repeated three times. The retentate (high molecular weight fraction) that contained the coffee melanoidins was freeze-dried and stored at −20 °C. The extraction yield of melanoidins was around 7.8 wt% of dry and defatted ground coffee.

2.3. Determination of carbohydrate, protein, and phenolic group contents

The total sugar content of coffee melanoidins was determined using the phenol-sulfuric acid method (Nielsen, 2010). Protein content (%, N × 5.5) was estimated using the Dumas method (Interscience Flash EA 1112 series, Thermo Scientific, Breda, The Netherlands) (Bekedam et al., 2006). Phenolic group content was measured using the Folin-Ciocalteu reagent, with chlorogenic acid as the standard (Singleton et al., 1965).

2.4. Adsorption kinetics

The interfacial tension between coffee melanoidins (or WPI) solution (0.1 g/L) and stripped rapeseed oil was recorded with an automated drop volume tensiometer (Tracker, Teclis, Longessaigne, France) by analyzing the axial symmetric shape (Laplace profile) of a rising oil drop (area: 40 mm^2) in the aqueous solution using a 20-gauge stainless steel needle (internal diameter, 0.603 mm; outer diameter, 0.908 mm). The interfacial tension (γ) was measured for 2 h at 20 °C, and the results were expressed as surface pressure ($\pi = \gamma_0 - \gamma$).

2.5. Preparation of coffee melanoidin-stabilized emulsions

Coffee melanoidins (0.25, 0.5, 1, 2, or 4 wt%) were dispersed in water and stirred overnight at 4 °C to ensure complete hydration. Coarse emulsions were prepared by homogenizing 90 wt% of the aqueous phase containing coffee melanoidins and 10 wt% of stripped rapeseed oil using a rotor-stator homogenizer (Ultra-turrax IKA T18 basic, Germany) at 11,000 rpm for 1 min. Final emulsions were prepared by passing the coarse emulsions through an M-110Y Microfluidizer (800 bar, 5 cycles) equipped with a F12Y interaction chamber (Microfluidics, Massachusetts, USA). The emulsions were partitioned as 3-g aliquots in polypropylene tubes (Eppendorf®,15 × 120 mm) and stored at room temperature (~20 °C) for 28 days. To prepare 4 wt% homogenized melanoidin solution, 4 wt% coffee melanoidins (without the addition of oil) were homogenized via a rotor-stator homogenizer and Microfluidizer under the same conditions as used for the emulsion preparation.

2.6. Physical stability of coffee melanoidin-stabilized emulsions

The particle size distribution, surface charge, and microstructural changes of emulsions were monitored over the storage time (at 0, 7, 14, 21, and 28 days) at room temperature (~20 °C).

Particle size distribution. The particle size distribution of emulsions was determined by static light scattering using a Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK) at 20 °C. The emulsions were diluted in water and stirred at 1400 rpm to prevent multiple scattering effects. The refractive index was set to 1.473 for rapeseed oil and 1.33 for water. The absorption index was set to 0.01.

Light microscopy. The microstructural changes of emulsions were monitored via an optical microscope (Carl Zeiss Axio Scope A1, Oberkochen, Germany). Emulsions were gently mixed prior to the observation. A drop of emulsions was then placed on a glass microscopy slide and covered with a cover slip. The microscopic images were taken using an objective magnification of 40 × . Some images were taken using a polarized light filter.

Viscosity. An Anton Paar rheometer (MCR502, Anton Paar GmbH, Graz, Austria) was used to determine the dynamic viscosity of the samples at 20 °C. For 0.25–2 wt% melanoidin-stabilized emulsions and 4 wt% homogenized melanoidin solution, a concentric cylinder system (DG 26.7, diameter: 26.662 mm, internal diameter: 24.655 mm, length: 40.000 mm) was used. Due to its gel structure, for 4 wt% melanoidin-stabilized emulsions, a plate-plate geometry (PP-25/P2, diameter: 25 mm) was used.

Droplet surface charge. The electrophoretic mobility of emulsions was measured by dynamic light scattering using a Zetasizer Ultra (Malvern Instruments LTD., Worcestershire, UK) in a disposable cuvette (DTS 1080) at 20 °C. Prior to the measurement, all emulsions were diluted 1000 times in water to minimize multiple scattering effects. The optical property settings were the same as those used for the particle size distribution measurement. Droplet surface charge (Zeta-potential) was calculated from the electrophoretic mobility using the Smoluchowski model (ZS Xplorer software).

2.7. Surface load

The surface load of the coffee melanoidin-stabilized emulsions was determined via two methods: (i) unadsorbed melanoidins in the continuous phase, and (ii) adsorbed melanoidins in the creamed phase. Prior to the surface load analysis, calibration curves to determine coffee melanoidin concentration were obtained by recording the absorption spectra (200–600 nm) of melanoidins (0.01–0.1 g/L) dispersed in water, or 1 wt% SDS solution using a DU 720 UV–visible spectrophotometer (Beckman Coulter, Woerden, the Netherlands).

Emulsions were centrifuged at 15,000×*g* for 1 h to separate the continuous phase and the creamed phase. To determine the surface load via the continuous phase, the continuous phase was collected by piercing a hole in the bottom of the centrifuge tubes. The concentration was determined according to calibration curves for melanoidins dispersed in water, and the surface load Γ_s (mg/m^2) was calculated according to equation (1):

$$\Gamma_s = \frac{C_a d_{3,2}}{6\varphi} \quad (1)$$

Where C_a (kg/m^3 water phase) corresponds to the concentration of the adsorbed coffee melanoidins, which was calculated by subtracting the concentration in the continuous phase from the concentration of the melanoidin solution used for emulsion preparation, $d_{3,2}$ (m) is the Sauter mean diameter of the fresh emulsions, and φ is the oil volume fraction.

To determine the surface load via the creamed phase, the concentration of the adsorbed coffee melanoidins and the oil content in the creamed phase were measured. The creamed phase obtained after centrifugation was collected and re-dispersed in water and centrifuged again as described earlier to remove any unadsorbed coffee melanoidins that may have been trapped between the oil droplets in the creamed phase after the first centrifugation. The resulting washed creamed phase was collected. An aliquot (0.2 g) of creamed phase was mixed with 3 g of water and 15 g of extraction solvent (hexane:isopropanol, 3:1, v/v). The mixture was then vortexed for 3 × 1 min and mixed in a rotator for 1 h, followed by centrifugation (3000×*g*, 5 min). The upper phase (hexane and oil) was collected and placed in the fume hood until the hexane evaporated, and the amount of oil remaining was weighed. Another aliquot of creamed phase was dispersed in a 1 wt% SDS solution and centrifuged at 15,000×*g* for 1 h. The adsorbed coffee melanoidins were displaced by SDS to the aqueous subnatant. The concentration of coffee melanoidins was then determined using the calibration curves for melanoidins dispersed in 1 wt% SDS. This value of C_a can directly be used in equation (1) to calculate the surface load Γ_s (mg/m^2).

2.8. Confocal laser scanning microscopy (CLSM)

Confocal laser scanning microscopy (CLSM) (Carl Zeiss, Jena, Germany) was used to further visualize the interfacial composition of the emulsion droplets. Proteins, polysaccharides, and lipids were fluorescently labelled with rhodamine B (10 μL/mL of sample, 1 mg/mL in water), calcofluor white (5 μL/mL of sample, 2 mg/mL in water), and BODIPY (10 μL/mL of sample, 1 mg/mL in ethanol), respectively. A small quantity of these emulsions was placed on a confocal microscope slide and gently covered with a cover slip. The excitation/emission wavelengths of rhodamine B, calcofluor white, and BODIPY were set at 543/580 nm, 405/450 nm, and 488/518 nm, respectively. Images of 512 × 512 pixels were obtained using a 100 × oil immersion objective.

2.9. Statistical analysis

All experiments were carried out at least in triplicate on samples that were prepared in duplicate in independent experiments. The results were reported as mean values ± standard deviations. The statistical analyses were carried out using one-way analysis of variance (ANOVA) using IBM SPSS statistics 23.0.0.2 (SPSS Inc, Chicago, Illinois, USA) with $P < 0.05$ being considered as significantly different.

3. Results and discussion

3.1. Characterization of coffee melanoidins

Absorption spectra. UV–visible absorption spectra of coffee melanoidins (placed in a 1-cm path length quartz cuvette) were recorded to confirm the extraction of melanoidins from coffee brews (Fig. S1). The spectra showed two absorption maxima at 280 and 325 nm and minor absorbance from 400 nm onward. This is in agreement with spectra reported previously (Bekedam et al., 2006): absorption at 280 nm has been linked to proteins, caffeine, chlorogenic acids, caffeic acid, and other complex polyphenolic molecules in the melanoidins, whereas absorption at 325 nm was mainly attributed to chlorogenic acid and caffeic acid (Bekedam et al., 2006; Lopes et al., 2016). Melanoidins have been reported to have a unique absorption signature at 405 and 420 nm, which was suggested to correspond to the core structure (405 nm) and the chromophore groups of melanoidins (420 nm) (Del Pino-García et al., 2012; Silván et al., 2010). To estimate the relative content of these compounds and compare the results to those in other research, the specific extinction coefficients (K_{mix}) at 280, 325, 405 and 420 nm were calculated based on the Lambert-Beer law (Table S1). The values of $K_{mix\ 280nm}$, $K_{mix\ 325nm}$, $K_{mix\ 405}$, and $K_{mix\ 420nm}$ were in line with the results reported previously (Bekedam et al., 2006, 2007).

Chemical composition. The composition of coffee melanoidins is ~70% carbohydrates, 12% protein, and 13% phenolics as shown in Table S2. The total carbohydrate content was consistent with the results reported by others (Bekedam et al., 2006; Tagliazucchi & Verzelloni, 2014). Mannose, galactose as well as arabinose are the most abundant sugars, indicating that galactomannans (~69%) and arabinogalactans (~28%) are the main polysaccharides in coffee melanoidins (Bekedam et al., 2006; Nunes & Coimbra, 2001). The protein content of 12% is similar to the results of Nunes and Coimbra (2001), although it is good to point out that the Dumas method may result in overestimation, since other non-protein nitrogen such as caffeine and trigonelline can also be detected. The phenolic group content (13%) is in line with Bekedam et al. (2006), who reported 15% of phenolic groups, confirming that phenolic groups are also largely incorporated into melanoidins.

Particle size distribution and light microscopy. The homogenization

process used for emulsion preparation (section 3.2) is expected to alter the particle size and possibly the charge (zeta potential) of coffee melanoidins dispersed in water. Therefore, this was investigated first. The initial particle size distribution of the dispersions was dominated by large aggregates/molecules in the micron range (≥10 μm) (Fig. 1A) with undefined shapes (Fig. S2A). Upon homogenization, the particle size decreased considerably (Fig. 1A & S2B), suggesting that the homogenization process causes disaggregation or disruption of melanoidin-based structures.

Zeta-potential. For both the original and homogenized melanoidin dispersions, the plots of the zeta-potential as function of pH overlap (Fig. 1B). The isoelectric point was around 2.5, close to the values reported for melanoidins prepared from glycine and glucose (Migo et al., 1997). At pH higher than 2.5, melanoidins were negatively charged, becoming more negative as pH increased (Fig. 1B), probably due to the presence of ferulic acid or caffeic acid moieties from chlorogenic acids (CGA) and uronic acids from arabinogalactans (Bekedam et al., 2008). At pH lower than 2.5, coffee melanoidins were slightly positively charged, probably because of the amino groups from proteins (Bekedam et al., 2008; Migo et al., 1997).

Surface activity. The surface pressure generated by melanoidins was measured at the rapeseed oil-water interface and compared with that obtained with whey protein isolate (WPI), a commonly used emulsifier. There was a rapid increase in surface pressure in the first 400 s, followed by a slower increase for both components, albeit that the surface pressure is higher (both initially and after 2 h of interfacial film aging) for WPI (Fig. 2).

Whey proteins are known to adsorb at the oil-water interface where they are next subjected to conformational rearrangements (Schröder et al., 2017). Regarding melanoidins, their surface activity might be due to the presence of amphipathic proteins, e.g., arabinogalactan proteins, galactomannans or protein-polyphenol complexes. Arabinogalactan proteins from green coffee beans have been shown to increase the surface pressure at air-water interface to ~22 mN/m, and they could easily adsorb at the interface to form a film (Redgwell et al., 2005) Garti and Reichman (1994) and Wu et al. (2009) found that galactomannans were able to reduce both the surface and interfacial tensions. After diffusing and adsorbing at the interface, the galactomannans could undergo a conformational change at the interface with a hydrophobic part anchoring to the oil phase and other parts extending to the water phase (Garti & Reichman, 1994).

Furthermore, it is expected that various components in coffee melanoidins (e.g., aggregates) are present as particles that contribute to interfacial stabilization via Pickering effects. The particle wettability, together with size geometry, and roughness, co-determines the strength of adhesion to the liquid-liquid interface. It is expected that there is considerable variation in these factors given the highly complex melanoidin mixture, and that the interplay of these factors ultimately leads to emulsion stabilization. In the next sections, the ability of the components to form and stabilize emulsions is therefore explored.

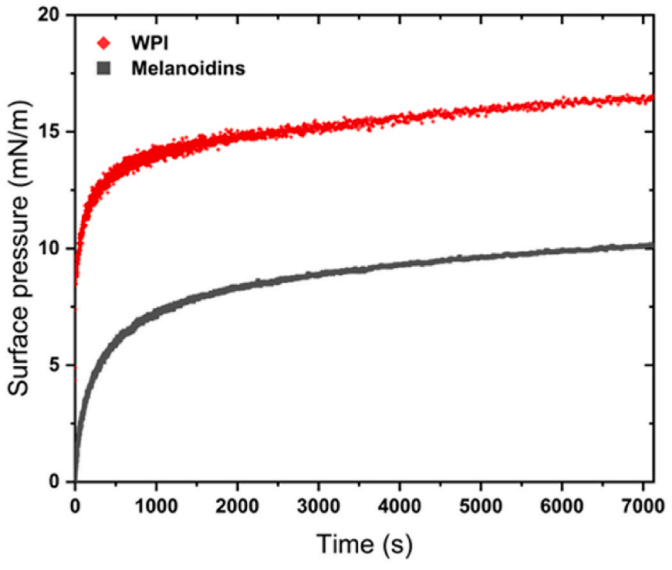

Fig. 1. Surface pressure of WPI and coffee melanoidins at a concentration of 0.1 g/L in water, at 20 °C.

3.2. Characterization of coffee melanoidin-stabilized emulsions

3.2.1. Emulsion appearance

Dispersions of coffee melanoidins in water with concentrations ranging from 0.25 to 4 wt% were used to prepare emulsions. Initially, all the emulsions had a brown, opaque, and homogeneous appearance (Fig. 3, inserts in A1-E1). All the fresh emulsions were fluid-like but were more viscous at increasing melanoidin concentration.

After 7 days of storage at room temperature, a visible creamed layer formed in emulsions containing 0.25–1 wt% melanoidins (Fig. 3, inserts of A2-C2), whereas the emulsions containing 2 and 4 wt% melanoidins showed a homogeneous appearance (Fig. 3, inserts of D2-E2). In addition, the 4 wt% melanoidin-stabilized emulsions gradually transformed from a liquid-like state to a gel-like appearance within a few days (Fig. 4, insert E). However, the emulsion gel was not strong and could easily be disrupted by agitation. Creaming rate is proportional to the square of the droplet size, and therefore creaming was expected for emulsions containing a low amount of melanoidins in which large droplets are present and the continuous phase has low viscosity (discussed further in sections 3.2.2 and 3.2.3). In the emulsions with higher continuous phase viscosity, the creaming rate is accordingly lower, and it may be reduced to zero if a weak gel is present.

After 28 days of storage, the creamed layer of the 0.25 wt% melanoidin-stabilized emulsions became more distinct, and the bottom serum layer became less opaque (Fig. 3, insets of A5). For the other emulsions, no significant change in appearance was observed after day 7. It is worth noting that no oil layer was formed (no oiling off) in all emulsions during storage.

3.2.2. Particle size distribution and emulsion morphology

At day zero, all emulsions exhibited a nearly monomodal size distribution, with sometimes a minor tail (Fig. 4, black curves). With increasing melanoidin concentration, the most prominent peak shifted to lower values resulting in a decrease in $d_{3,2}$ from 0.42 μm to 0.06 μm (Fig. 4).

For 0.25 wt% melanoidin-based emulsions, some droplets were loosely connected (Fig. 3A1); whereas for 0.5 wt% melanoidin-based emulsions, slight flocculation was observed (Fig. 3B1). At these relatively low concentrations, the amount of melanoidins at the interface is probably not sufficient to cover the surface of all oil droplets, resulting in bridging flocculation (with melanoidins shared between droplets), and possibly coalescence (Berton-Carabin et al., 2018; Guzey & McClements, 2006). At 0.5 wt% melanoidin concentrations and higher, the emulsions became microscopically homogeneous (Fig. 3C1-E1). After 7 days of storage, emulsions containing 0.25 and 0.5 wt% melanoidins experienced more flocculation and coalescence, and those containing 1 wt% melanoidins also started to flocculate (Fig. 3A2-C2). This is reflected in the occurrence of a small shoulder/peak in Fig. 4. At longer storage times, a second peak appeared at larger sizes, that continued to increase in time, whereas the contribution of the smaller droplets decreased in these emulsions (Fig. 4A–C), leading to further destabilization.

Emulsions stabilized with 2 wt% melanoidins were more stable than other emulsions. The particle size distribution was rather constant for 2 weeks, exhibiting a monomodal distribution with a small tail (Fig. 4D). After 3 weeks of storage, a second peak ranging from 1 to 100 μm appeared as a result of flocculation (Fig. 3D4-D5), which remained unchanged until the end of the experiments (Fig. 4D). In 4 wt%

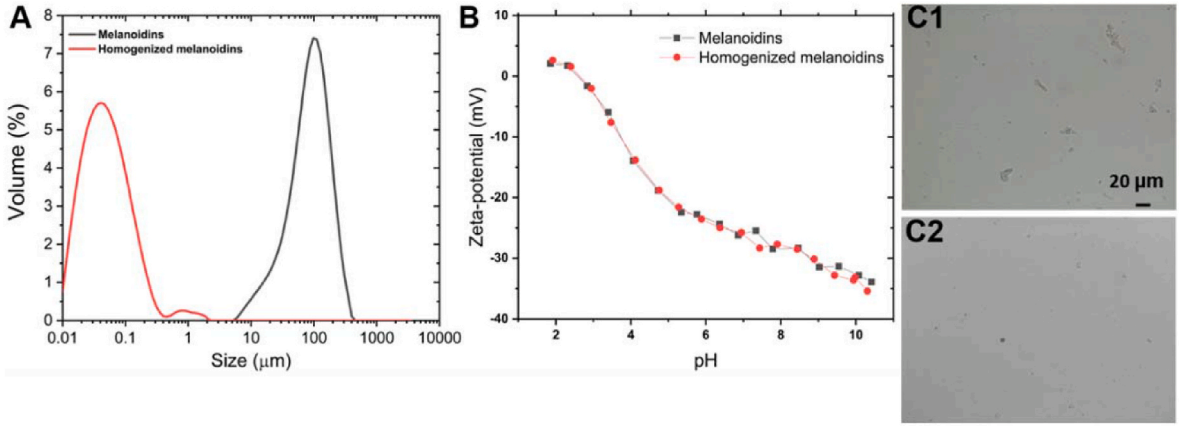

Fig. 2. Particle size distribution (A) and zeta-potential (B) of coffee melanoidins and homogenized coffee melanoidins dispersed in water, and microscopic pictures of these dispersions (C1, C2, respectively).

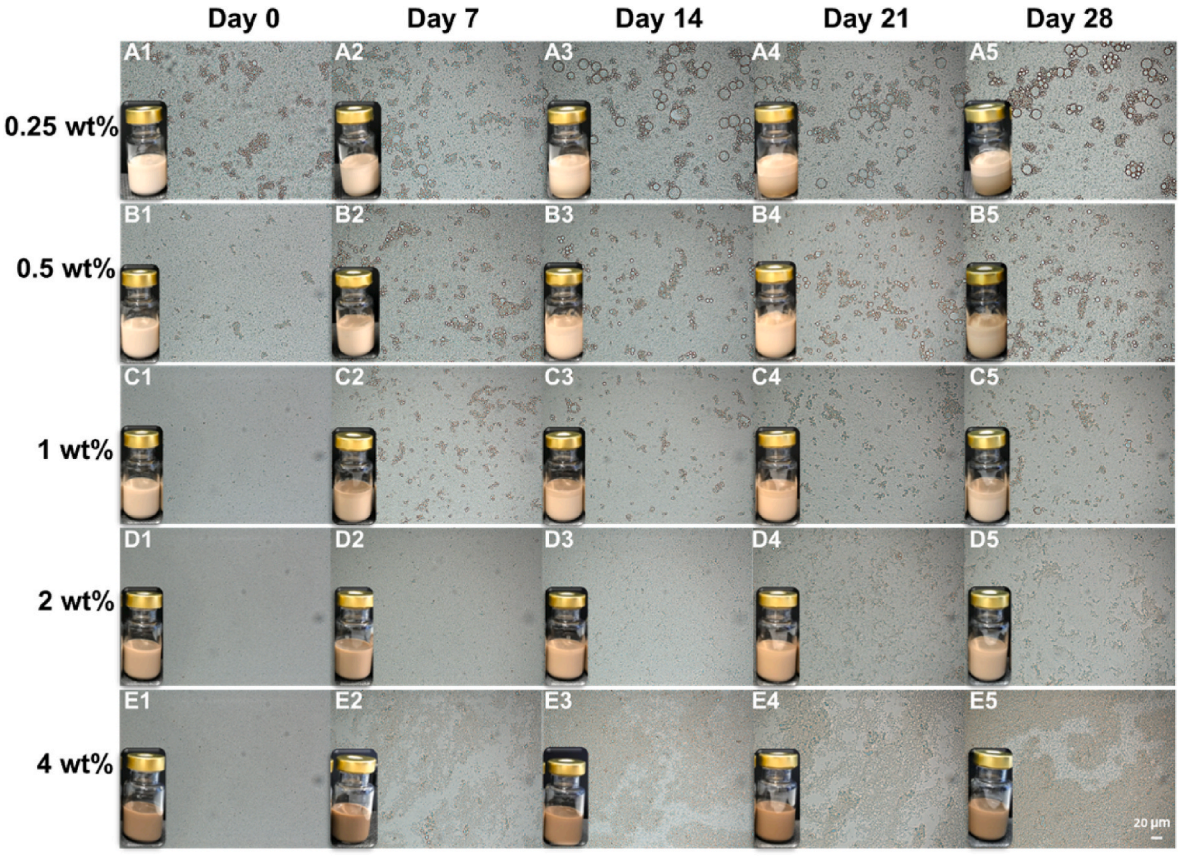

Fig. 3. Microscopic pictures of emulsions stabilized with 0.25 (A), 0.5 (B), 1 (C), 2 (D), and 4 wt% (E) coffee melanoidins stored at room temperature for 0 (1), 7 (2), 14 (3), 21 (4), and 28 days (5). All images are at the same magnification (scale bar - shown on panel E5 - is 20 μm). Inserts are macroscopic images of the emulsions.

melanoidin-stabilized emulsions, aggregated droplets formed (Fig. 3E2) and a large-sized peak appeared (Fig. 4E) after 7 days of storage, which dramatically increased with time, whereas the original small peak disappeared (Fig. 4E). As mentioned, and also illustrated by the upside-down tube in Fig. 4E, wt% melanoidin-stabilized emulsions gradually formed gel-like structures upon storage. Also others have found the formation of gel-like structures at high amounts of galactomannans (N. Garti et al., 1997; Wu et al., 2009). In the next section dedicated to viscosity, it is investigated whether the gel formation is due to the melanoidins as such, or to their interaction with the oil droplets.

3.2.3. *Viscosity*

We determined the apparent viscosity of the homogenized melanoidin solution with the highest concentration (4 wt%), and of all emulsions as a function of shear (Fig. 5). The viscosity profile of the 4 wt % homogenized melanoidin solution was constant and similar to that measured for the 0.25 wt% melanoidin-stabilized emulsion. The viscosity of emulsions with >0.25 wt% melanoidins increased with melanoidin concentration and decreased with increasing shear rate, showing typical shear thinning behavior that was more pronounced at higher melanoidin concentrations. This indicates that network formation involves melanoidins and droplets, and does not occur in a concentrated

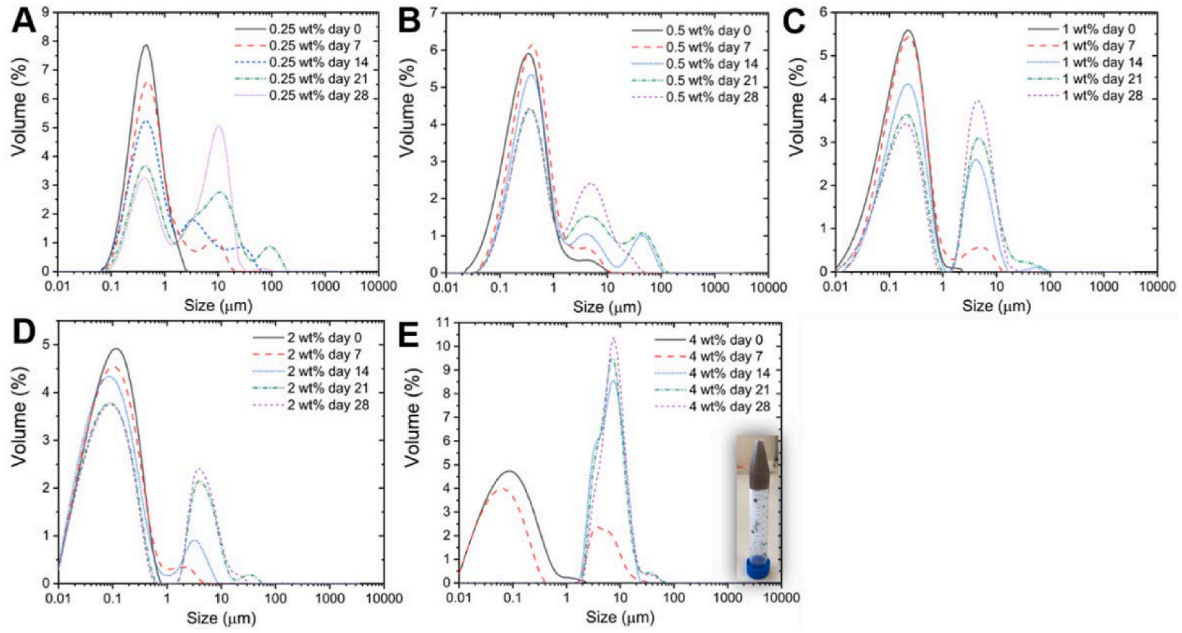

Fig. 4. Droplet size distribution of emulsions stabilized with 0.25 (A), 0.5 (B), 1 (C), 2 (D), and 4 wt% (E) of coffee melanoidins. Insert in panel E, the gelled emulsion after 7 days of storage.

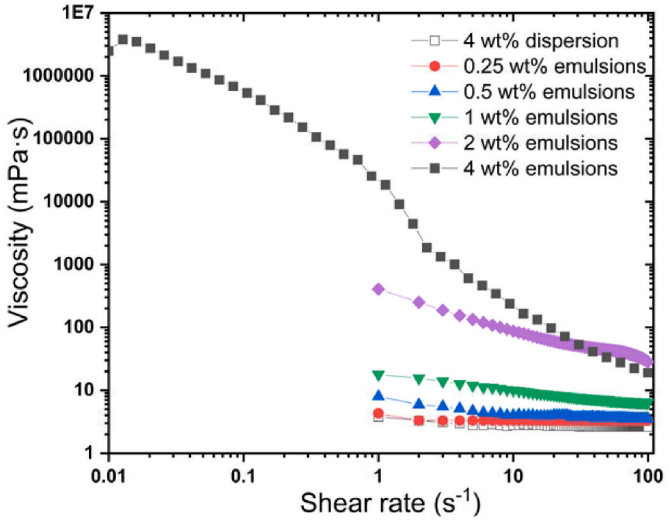

Fig. 5. Apparent viscosity as a function of applied shear rate of the 4 wt% homogenized melanoidin solution (hollow) and of O/W emulsions (10 wt% oil) stabilized with 0.25–4 wt% melanoidins (solid).

pure melanoidin dispersion. Data also showed that a threshold concentration of melanoidins is needed for network formation to take place in the O/W emulsions.

The shear-thinning behavior of the emulsions can be attributed to the disintegration of the network involving droplets and melanoidins, and realignment of the droplets upon shearing, resulting in a decrease in the resistance to flow (Ali Al-Maqtari et al., 2021; Ye et al., 2016). For the emulsion with 4 wt% melanoidins, the network was strong (section 3.2.2), forming a gelled structure with high viscosity (Fig. 5) that could carry its own weight. It is interesting to note that melanoidins and oil droplets (with low dispersed fraction, 10 wt%) did not give a high viscosity on their own. Instead, the presence of large amounts of melanoidins in the continuous phase may induce flocculation to form a self-supporting emulsion gel (Dickinson, 2003). In addition, it is also possible that some components of the melanoidins (e.g., covalently linked phenolic compounds, proteins, and/or polysaccharides) may be cross-linking the surface layer between adjacent droplets and/or the excess melanoidins in the continuous phase, which could also result in network formation in emulsions. Huang et al. (2019) reported that insoluble soybean fiber (ISF, 0.4 wt%) was able to improve the stability of low-concentration soy protein isolate (0.4 wt%) emulsions (10 wt% soybean oil) via the formation of flocculated droplets and a gel-like network. Similarly, the apparent viscosity of ISF suspension (1 wt%, prepared using a rotor-stator at 10,000 rpm for 2 min) was low and constant (~3 mPa s) with for shear rates from 0 to 100 s-1 (Chen et al., 2019).

3.2.4. *Surface charge of emulsion droplets*

The surface charge of the oil droplets was assessed through the zeta-potential (Fig. 6). All emulsions had a negative surface charge. The zeta-potential increased from −48 mV to −38 mV (Fig. 6), going from melanoidin concentration 0.25 to 4 wt%, and the pH value decreased from 7 to 5.5 (Fig. S3). These zeta-potentials were much higher than those

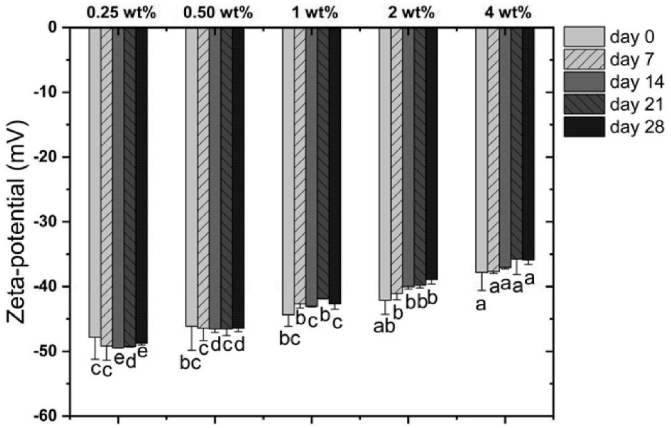

Fig. 6. Zeta-potential of the coffee melanoidin-stabilized emulsion droplets. Small letters are for comparison among the emulsions with different melanoidin concentrations on the same day. Different letters indicate significant differences ($P < 0.05$).

measured in a pure melanoidins solution (Fig. 2), which may be due to the presence of charged groups at the droplet surface or due to the rearrangement of melanoidins at the interface leading to the exposure of negatively charged groups. For each emulsion, no significant change in zeta-potential was observed upon 28 days of storage ($P > 0.05$).

In general, electrostatic repulsion between droplets is considered substantial enough to ensure emulsion stability when the magnitude of zeta-potential is greater than 30 mV (Dukhin & Goetz, 1998), which all our emulsions had (Fig. 6). However, our 0.25 wt% melanoidin-stabilized emulsion (−48 mV) was not physically stable, indicating that also other destabilizing factors were playing a role, probably due to limited emulsifier availability.

3.2.5. Surface load

The surface load of the fresh emulsions was estimated via either the creamed phase or the continuous phase of the emulsions (Fig. 7). For both methods, the surface load slightly decreased and then increased with increasing melanoidin concentration. The continuous phase method (Fig. 7B) gave higher surface loads than the creamed phase method (Fig. 7A), which is in agreement with the investigations of Hinderink et al. (2021) for pea protein-stabilized emulsions. The continuous phase method is widely used but precipitated components are not accounted for appropriately, leading to overestimation of the surface load. Therefore, the creamed phase method was considered more reliable for our systems.

The surface load of the melanoidin-stabilized emulsions ranged from 0.3 to 0.6 mg/m^2 (Fig. 7A), which is relatively low compared to protein-stabilized emulsions (generally around 1–3 mg/m^2) but similar to values found for other polysaccharide-stabilized emulsions (e.g., 0.4–0.9 mg/m2 (Mikkonen et al., 2016):). These results hint that polysaccharide-rich fractions from coffee melanoidins might be more likely to accumulate at the oil-water surface, a hypothesis which was further investigated by CLSM.

3.2.6. Confocal laser scanning microscope (CLSM) and polarized light microscope

As emulsions with large enough droplets are needed to give insightful images in CLSM, fresh emulsions stabilized with 0.25 wt% melanoidins were chosen for this study (i.e., the system with the largest droplets) (Fig. 8). Most of the oil droplets (labelled in red) were connected with each other in clusters, which confirms the light microscopy results (Fig. 3). Polysaccharides (labelled in green) encircled the oil droplets (Fig. 8 A&B), whereas proteins (labelled in teal) were mainly detected in the continuous phase (Fig. 8C), suggesting that polysaccharide-rich fractions from the melanoidins were predominantly present at the interface. To confirm this finding, 1 wt% melanoidin-stabilized coarse emulsions (prepared via rotor-stator homogenization only) were prepared and investigated, and similar results were found (Fig. S4). Other studies also found that in polysaccharide-rich samples, the protein components did not play a significant role in stabilizing emulsions (Garti & Reichman, 1994; Mikkonen et al., 2009; Wu et al., 2009). Nissim Garti and Reichman (1994) even found that purified guar gum (protein content reduced to 0.8 wt%) had higher surface activity than the original gum, and they suggested that the protein fraction may not be surface-active.

When observing the emulsions with polarized light microscopy (Fig. 8D and E), both emulsions showed distinctive rings on the oil droplets, and that could be related to accumulation of galactomannan fractions at the oil-water interface, as was observed for other galactomannan-stabilized emulsions (Garti & Reichman, 1993, 1994).

4. Conclusions

This work demonstrates that naturally-occurring coffee melanoidins are capable of stabilizing O/W emulsions without the need of other stabilizers. Fresh emulsions stabilized with 0.25–4 wt% melanoidins, prepared by high pressure homogenization had a brown, opaque, and homogeneous appearance with a nearly monomodal size distribution. Upon 28 days of storage at room temperature (~20 °C), emulsions stabilized with 0.25–1 wt% melanoidins underwent creaming and showed some droplet flocculation and possibly coalescence. The emulsion stabilized by 2 wt% melanoidins showed high physical stability, and the one prepared with 4 wt% melanoidins gradually transformed from liquid-like to gel-like state due to network formation between droplets and melanoidins.

Coffee melanoidins can reduce the oil-water interfacial tension, induce electrostatic repulsion between emulsion droplets, and may form a weak network that contributes to emulsion stability. In particular, the polysaccharide-rich fractions from the melanoidins are present at the interface, at the expense of the protein-rich fractions, as deduced from CLSM and polarized light microscopy.

This study showed that coffee melanoidins exhibit great potential to formulate clean label food-grade emulsions. From a practical perspective, the flavor and color of coffee melanoidin ingredients would need to be considered and/or mitigated, yet we expect that they could be ingredients relevant to targeted food products (e.g., baked goods, plant-based dairy products). More in general, this work suggests that Maillard reaction products available from food by-products (such as melanoidins from spent ground coffee or roasted cocoa shells) can contribute to sustainable and economically feasible food design (Bondam et al., 2022; Gemechu, 2020; Sharma et al., 2021). Further work should be directed toward the capability of coffee melanoidins to act as dual-function ingredients (i.e., emulsifiers with antioxidant properties to also improve the oxidative stability of emulsions).

Author contributions

Jilu Feng: Conceptualization, Methodology, Validation, Formal

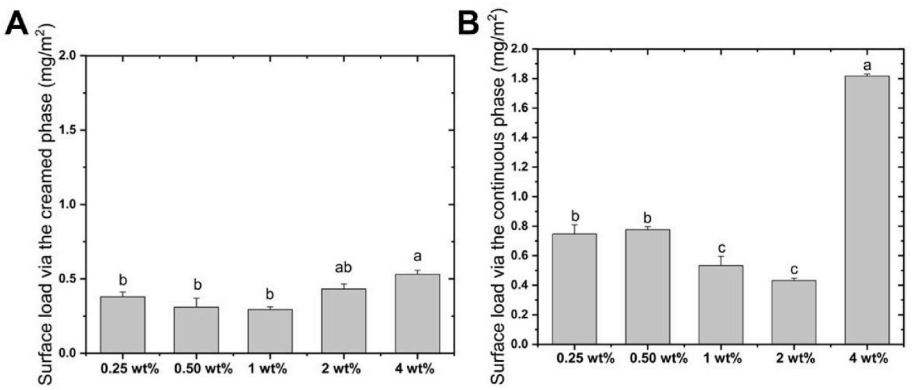

Fig. 7. Surface load of the coffee melanoidin-stabilized emulsions measured via the creamed phase (A) or the continuous phase (B).

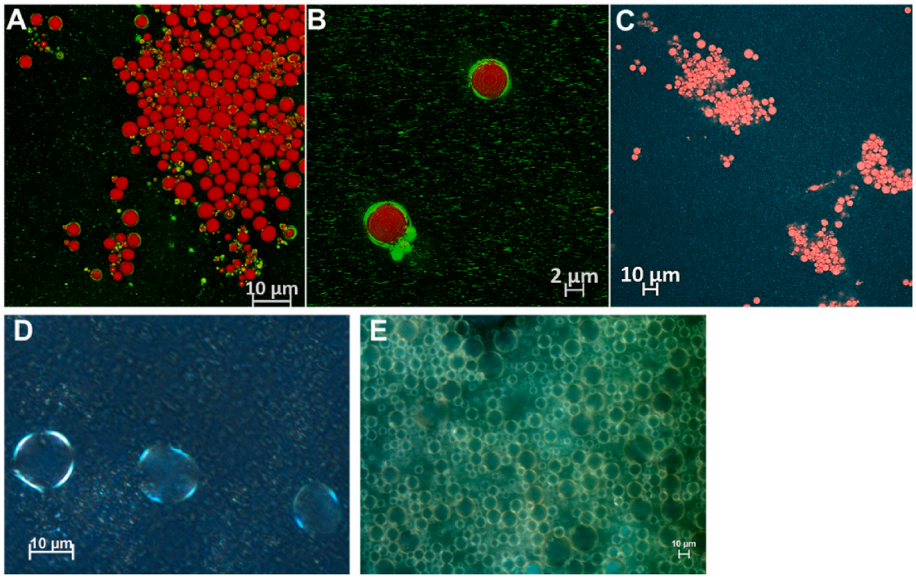

Fig. 8. Confocal micrographs of emulsions stabilized with 0.25 wt% coffee melanoidins (A–C). Green color represents polysaccharides (stained by calcofluor white), teal color represents proteins (stained by Rhodamine B), and red color represents oil (stained by BODIPY). Polarized light microscopy images of emulsions prepared by (D) high pressure homogenization, using 0.25 wt% melanoidins, or (E) rotor-stator homogenization, using 1 wt% melanoidins.

analysis, Investigation, Data Curation, Writing - Original Draft, Visualization. Claire C. Berton-Carabin: Conceptualization, Methodology, Writing - Review & Editing, Visualization, Supervision. Sylvain Guyot: Methodology, Writing - Review & Editing, Visualization. Agnès Gacel: Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Review & Editing, Visualization. Vincenzo Fogliano: Conceptualization, Methodology, Writing - Review & Editing, Visualization, Supervision. Karin Schroën: Conceptualization, Methodology, Writing - Review & Editing, Visualization, Supervision.

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.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2023.108522.

References

Ali Al-Maqtari, Q., Ghaleb, A. D. S., Ali Mahdi, A., Al-Ansi, W., Essam Noman, A., Wei, M., Aladeeb, A., & Yao, W. (2021). Stabilization of water-in-oil emulsion of Pulicaria jaubertii extract by ultrasonication: Fabrication, characterization, and storage stability. *Food Chemistry, 350*(February), Article 129249. https://doi.org/10.1016/j.foodchem.2021.129249

Bekedam, E. K., De Laat, M. P. F. C., Schols, H. A., Van Boekel, M. A. J. S., & Smit, G. (2007). Arabinogalactan proteins are incorporated in negatively charged coffee brew melanoidins. *Journal of Agricultural and Food Chemistry, 55*(3), 761–768. https://doi.org/10.1021/jf063010d

Bekedam, E. K., Schols, H. A., Van Boekel, M. A. J. S., & Smit, G. (2006). High molecular weight melanoidins from coffee brew. *Journal of Agricultural and Food Chemistry, 54*(20), 7658–7666. https://doi.org/10.1021/jf0615449

Bekedam, E. K., Schols, H. A., Van Boekel, M. A. J. S., & Smit, G. (2008). Incorporation of chlorogenic acids in coffee brew melanoidins. *Journal of Agricultural and Food Chemistry, 56*(6), 2055–2063. https://doi.org/10.1021/jf073157k

Berton, C., Genot, C., & Ropers, M. (2011). Quantification of unadsorbed protein and surfactant emulsifiers in oil-in-water emulsions. *Journal of Colloid and Interface Science, 354*(2), 739–748. https://doi.org/10.1016/j.jcis.2010.11.055

Berton-Carabin, C. C., Sagis, L., & Schroën, K. (2018). Formation, structure, and functionality of interfacial layers in food emulsions. *Annual Review of Food Science and Technology, 9*(1), 551–587. https://doi.org/10.1146/annurev-food-030117-012405

Berton-Carabin, C. C., & Schroën, K. (2015). Pickering emulsions for food applications: Background, trends, and challenges. *Annual Review of Food Science and Technology, 6*(1), 263–297. https://doi.org/10.1146/annurev-food-081114-110822

Bondam, A. F., Diolinda da Silveira, D., Pozzada dos Santos, J., & Hoffmann, J. F. (2022). Phenolic compounds from coffee by-products: Extraction and application in the food and pharmaceutical industries. *Trends in Food Science & Technology, 123*, 172–186. https://doi.org/10.1016/j.tifs.2022.03.013

Borrelli, R. C., Visconti, A., Mennella, C., Anese, M., & Fogliano, V. (2002). Chemical characterization and antioxidant properties of coffee melanoidins. *Journal of Agricultural and Food Chemistry, 50*(22), 6527–6533. https://doi.org/10.1021/jf025686o

Chen, B., Cai, Y., Liu, T., Huang, L., Deng, X., Zhao, Q., & Zhao, M. (2019). Improvements in physicochemical and emulsifying properties of insoluble soybean fiber by physical-chemical treatments. *Food Hydrocolloids, 93*(July 2018), 167–175. https://doi.org/10.1016/j.foodhyd.2019.01.058

D'Agostina, A., Boschin, G., Bacchini, F., & Arnoldi, A. (2004). Investigations on the high molecular weight foaming fractions of espresso coffee. *Journal of Agricultural and Food Chemistry, 52*(23), 7118–7125. https://doi.org/10.1021/jf049013c

Del Pino-García, R., González-Sanjosé, M. L., Rivero-Pérez, M. D., & Muñiz, P. (2012). Influence of the degree of roasting on the antioxidant capacity and genoprotective effect of instant coffee: Contribution of the melanoidin fraction. *Journal of Agricultural and Food Chemistry, 60*(42), 10530–10539. https://doi.org/10.1021/jf302747v

Dickinson, E. (2003). Hydrocolloids at interfaces and the influence on the properties of dispersed systems. *Food Hydrocolloids, 17*(1), 25–39. https://doi.org/10.1016/S0268-005X(01)00120-5

Dukhin, A. S., & Goetz, P. J. (1998). Characterization of aggregation phenomena by means of acoustic and electroacoustic spectroscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 144*(1–3), 49–58. https://doi.org/10.1016/S0927-7757(98)00565-2

Fogliano, V., & Morales, F. J. (2011). Estimation of dietary intake of melanoidins from coffee and bread. *Food & Function, 2*(2), 117–123. https://doi.org/10.1039/c0fo00156b

Friedman, M. (1996). Food browning and its prevention: An overview. *Journal of Agricultural and Food Chemistry, 44*(3). https://doi.org/10.1021/jf950394r

Garti, N., Madar, Z., Aserin, A., & Sternheim, B. (1997). Fenugreek galactomannans as food emulsifiers. *LWT - Food Science and Technology, 30*(3), 305–311. https://doi.org/10.1006/fstl.1996.0179

Garti, N., & Reichman, D. (1993). Food structure hydrocolloids as food emulsifiers and stabilizers. *Food Structure, 12*(4), 411–426.

Garti, N., & Reichman, D. (1994). Surface properties and emulsification activity of galactomannans. *Food Hydrocolloids, 8*(2), 155–173. https://doi.org/10.1016/S0268-005X(09)80041-6

Gemechu, F. G. (2020). Embracing nutritional qualities, biological activities and technological properties of coffee byproducts in functional food formulation. *Trends in Food Science & Technology, 104*, 235–261. https://doi.org/10.1016/j.tifs.2020.08.005

Guzey, D., & McClements, D. J. (2006). Formation, stability and properties of multilayer emulsions for application in the food industry. *Advances in Colloid and Interface Science, 128–130*(2006), 227–248. https://doi.org/10.1016/j.cis.2006.11.021

Higdon, J. V., & Frei, B. (2006). Coffee and health: A review of recent human research. *Critical Reviews in Food Science and Nutrition, 46*(2), 101–123. https://doi.org/10.1080/10408390500400009

Hinderink, E. B. A., Sagis, L., Schroën, K., & Berton-Carabin, C. C. (2021). Sequential adsorption and interfacial displacement in emulsions stabilized with plant-dairy protein blends. *Journal of Colloid and Interface Science, 583*, 704–713. https://doi.org/10.1016/j.jcis.2020.09.066

Huang, L., Cai, Y., Liu, T., Zhao, X., Chen, B., Long, Z., Zhao, M., Deng, X., & Zhao, Q. (2019). Stability of emulsion stabilized by low-concentration soybean protein isolate: Effects of insoluble soybean fiber. *Food Hydrocolloids, 97*(July), Article 105232. https://doi.org/10.1016/j.foodhyd.2019.105232

Lopes, G. R., Ferreira, A. S., Pinto, M., Passos, C. P., Coelho, E., Rodrigues, C., Figueira, C., Rocha, S. M., Nunes, F. M., & Coimbra, M. A. (2016). Carbohydrate content, dietary fibre and melanoidins: Composition of espresso from single-dose coffee capsules. *Food Research International, 89*, 989–996. https://doi.org/10.1016/j.foodres.2016.01.018

McClements, D. J. (2005). *Food emulsions: Principles, practices, and techniques*. Boca Raton: CRC Press. Boca Raton: CRC Press.

Migo, V. P., Del Rosario, E. J., & Matsumura, M. (1997). Flocculation of melanoidins induced by inorganic ions. *Journal of Fermentation and Bioengineering, 83*(3), 287–291. https://doi.org/10.1016/S0922-338X(97)80994-4

Mikkonen, K. S., Tenkanen, M., Cooke, P., Xu, C., Rita, H., Willför, S., Holmbom, B., Hicks, K. B., & Yadav, M. P. (2009). Mannans as stabilizers of oil-in-water beverage emulsions. *LWT - Food Science and Technology, 42*(4), 849–855. https://doi.org/10.1016/j.lwt.2008.11.010

Mikkonen, K. S., Xu, C., Berton-Carabin, C., & Schroën, K. (2016). Spruce galactoglucomannans in rapeseed oil-in-water emulsions: Efficient stabilization performance and structural partitioning. *Food Hydrocolloids, 52*, 615–624. https://doi.org/10.1016/j.foodhyd.2015.08.009

Moreira, A. S. P., Nunes, F. M., Domingues, M. R., & Coimbra, M. A. (2012). Coffee melanoidins: Structures, mechanisms of formation and potential health impacts. *Food & Function, 3*(9), 903–915. https://doi.org/10.1039/c2fo30048f

Moreira, A. S. P., Nunes, F. M., Domingues, M. R. M., & Coimbra, M. A. (2014). *Galactomannans in coffee. Coffee in Health and disease prevention* (pp. 173–183). https://doi.org/10.1016/B978-0-12-409517-5.00019-X

Nielsen, S. S. (2010). Phenol-sulfuric acid method for total carbohydrates. In S. S. Nielsen (Ed.), *Food analysis laboratory manual* (pp. 47–53). Springer US. https://doi.org/10.1007/978-1-4419-1463-7_6.

Nunes, F. M., & Coimbra, M. A. (1998). Influence of polysaccharide composition in foam stability of espresso coffee. *Carbohydrate Polymers, 37*(3), 283–285. https://doi.org/10.1016/S0144-8617(98)00072-1

Nunes, F. M., & Coimbra, M. A. (2001). Chemical characterization of the high molecular weight material extracted with hot water from green and roasted arabica coffee. *Journal of Agricultural and Food Chemistry, 49*(4), 1773–1782. https://doi.org/10.1021/jf0012953

Nunes, F. M., Cruz, A. C. S., & Coimbra, M. A. (2012). Insight into the mechanism of coffee melanoidin formation using modified “in Bean” models. *Journal of Agricultural and Food Chemistry, 60*(35), 8710–8719. https://doi.org/10.1021/jf301527e

Piazza, L., Gigli, J., & Bulbarello, A. (2008). Interfacial rheology study of espresso coffee foam structure and properties. *Journal of Food Engineering, 84*(3), 420–429. https://doi.org/10.1016/j.jfoodeng.2007.06.001

Redgwell, R. J., Schmitt, C., Beaulieu, M., & Curti, D. (2005). Hydrocolloids from coffee: Physicochemical and functional properties of an arabinogalactan-protein fraction from green beans. *Food Hydrocolloids, 19*(6), 1005–1015. https://doi.org/10.1016/j.foodhyd.2004.12.010

Schröder, A., Berton-Carabin, C., Venema, P., & Cornacchia, L. (2017). Interfacial properties of whey protein and whey protein hydrolysates and their influence on O/W emulsion stability. *Food Hydrocolloids, 73*, 129–140. https://doi.org/10.1016/j.foodhyd.2017.06.001

Sharma, A., Ray, A., & Singhal, R. S. (2021). A biorefinery approach towards valorization of spent coffee ground: Extraction of the oil by supercritical carbon dioxide and utilizing the defatted spent in formulating functional cookies. *Future Foods, 4*, Article 100090. https://doi.org/10.1016/j.fufo.2021.100090

Silván, J. M., Morales, F. J., & Saura-Calixto, F. (2010). Conceptual study on maillardized dietary fiber in coffee. *Journal of Agricultural and Food Chemistry, 58*(23), 12244–12249. https://doi.org/10.1021/jf102489u

Singleton, V. L., Rossi, J. A., & Jr, J. (1965). Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *American Journal of Enology and Viticulture, 16*(3), 144–158.

Tagliazucchi, D., & Verzelloni, E. (2014). Relationship between the chemical composition and the biological activities of food melanoidins. *Food Science and Biotechnology, 23*(2), 561–568. https://doi.org/10.1007/s10068-014-0077-5

Walker, J. M., Mennella, I., Ferracane, R., Tagliamonte, S., Holik, A. K., Hölz, K., Somoza, M. M., Somoza, V., Fogliano, V., & Vitaglione, P. (2020). Melanoidins from coffee and bread differently influence energy intake: A randomized controlled trial of food intake and gut-brain axis response. *Journal of Functional Foods, 72*(May). https://doi.org/10.1016/j.jff.2020.104063

Wu, Y., Cui, W., Eskin, N. A. M., & Goff, H. D. (2009). An investigation of four commercial galactomannans on their emulsion and rheological properties. *Food Research International, 42*(8), 1141–1146. https://doi.org/10.1016/j.foodres.2009.05.015

Ye, F., Miao, M., Cui, S. W., Jiang, B., Jin, Z., & Li, X. (2016). Characterisations of oil-in-water Pickering emulsion stabilized hydrophobic phytoglycogen nanoparticles. *Food Hydrocolloids, 76*, 78–87. https://doi.org/10.1016/j.foodhyd.2017.05.003

Zhang, H., Zhang, H., Troise, A. D., & Fogliano, V. (2019). Melanoidins from coffee, cocoa, and bread are able to Scavenge α-Dicarbonyl compounds under simulated physiological conditions. *Journal of Agricultural and Food Chemistry, 67*(39), 10921–10929. https://doi.org/10.1021/acs.jafc.9b03744