Food Hydrocolloids 74 (2018) 239–248

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Characterization of Pickering emulsion gels stabilized by zein/gum arabic complex colloidal nanoparticles

Lei Dai, Cuixia Sun, Yang Wei, Like Mao, Yanxiang Gao*

Beijing Advanced Innovation Center for Food Nutrition and Human Health, Beijing Laboratory for Food Quality and Safety, Beijing Key Laboratory of Functional Food from Plant Resources, College of Food Science & Nutritional Engineering, China Agricultural University, Beijing, 100083, PR China

ARTICLE INFO

Article history:
Received 5 June 2017
Received in revised form
31 July 2017
Accepted 31 July 2017
Available online 1 August 2017

Keywords:
Zein/gum arabic complex nanoparticles
Pickering emulsion gels
Wettability
Microstructure
Rheological property

ABSTRACT

Recently, Pickering emulsions have attracted extensive interests due to their advantages of "surfactant-free" and sustained delivery for bioactives. However, developing natural, biodegradable and food grade nanoparticles as Pickering emulsion stabilizers face new challenges. In this study, zein/gum arabic (GA) complex colloidal nanoparticles (ZGAPs) were prepared with a core-shell structure through hydrogen bonding and electrostatic interactions. The mean size of ZGAPs was larger than that of zein nanoparticles, and the zeta potential reversed from positive to negative, further confirming that GA molecules adsorbed onto the surface of zein nanoparticles. The three-phase contact angle ($\theta_{o/w}$) of zein nanoparticles was around 133.75°. After addition of GA, the $\theta_{o/w}$ of ZGAPs was adjusted to 88.95° closing to neutral wettability. This result indicated that ZGAPs could be developed as effective Pickering emulsifiers. Confocal laser scanning microscope images evidenced that ZGAPs formed a densely packed layer at the surface of oil droplets, which provided compact barriers of the droplets against coalescence and Ostwald ripening. At constant particle concentrations, the oil volume fraction significantly influenced the droplet sizes and rheological properties of Pickering emulsions. The droplet size and emulsified phase volume fraction of Pickering emulsions were increased with the rise of oil fraction. Consequently, Pickering emulsion gels were successfully fabricated at a higher oil fraction $\varphi \geq 0.5$, which exhibited a long-term storage stability. These findings would provide a potential way of producing Pickering emulsion gels, which showed the advantages of both emulsions and gels, and could become novel and effective delivery systems of bioactives.

1. Introduction

Emulsions based delivery systems have wide applications in the encapsulation and delivery of bioactive compounds in food industry for protecting therm against chemical degradation, enhancing bioavailability and controlled release (McClements, 2012). Conventional emulsions were stabilized by biopolymers (polysaccharides and proteins) and low molecular weight emulsifiers through forming steric elastic film or reducing the interfacial tension (Feng & Lee, 2016; Xiao, Li, & Huang, 2016). Compared to conventional emulsions, Pickering emulsions, which stabilized the oil–water interface by colloidal particles, have attracted extensive interests in recent years due to their advantages of "surfactant-free", high stability against coalescence and Ostwald ripening (Xiao, Wang, Gonzalez, & Huang, 2016). The colloidal particles could irreversibly adsorb and anchor at the oil/water interface and formed a rigid steric barrier of compact layer to stabilize Pickering emulsions (Hu et al., 2016).

Recently, studies on the Pickering emulsion stabilizers were mainly focused on the inorganic particles, such as calcium carbonate (Binks, Muijlwijk, Koman, & Poortinga, 2017), laponite clay (Ashby & Binks, 2000), silica (Zhao, Dan, Pan, Nitin, & Tikekar, 2013) and so on. However, in consideration of the environmental and food safety problems, the inorganic particles were not wise choices and had limited applicability in food industry (de Folter, van Ruijven, & Velikov, 2012). Therefore, developing natural, environmentally-friendly, biodegradable and food grade colloidal particles stabilized Pickering emulsions became a key scientific problem demanding to be promptly solved (Song et al., 2015). Certain food grade particles were testified to have better effects on stabilizing oil-in-water (O/W) emulsions, for instance, cellulose

* Corresponding author. Box 112, No. 17 Qinghua East Road, Haidian District, Beijing 100083, China.
E-mail address: gyxcau@126.com (Y. Gao).

http://dx.doi.org/10.1016/j.foodhyd.2017.07.040
0268-005X/© 2017 Published by Elsevier Ltd.

nanocrystals (Cherhal, Cousin, & Capron, 2016), modified starch (Song et al., 2015), soy glycinin (Liu & Tang, 2016a, b) and prolamin (Xiao, Wang et al., 2016; Hu et al., 2016; Zou, Guo, Yin, Wang, & Yang, 2015).

Zein, the major storage protein of corn, is generally regarded as safe (GRAS) food ingredient by the US Food and Drug Administration (Patel, Bouwens, & Velikov, 2010). Due to the high surface hydrophobicity, zein can easily form colloidal nanoparticles by self-assembly. Therefore, zein particles was used as a potential food grade Pickering emulsion stabilizer. De Folter et al., (2012) reported that zein colloidal particles fabricated through anti-solvent precipitation procedure could produce surfactant-free O/W Pickering emulsions with droplet sizes in the range 10–200 μm. However, zein Pickering emulsions was unstable due to the poor wettability of zein colloidal particles (Feng & Lee, 2016; Wang et al., 2015). The colloidal particles used to fabricate Pickering emulsions should have an appropriate wettability, which was the key factor influencing the formation and stability of Pickering emulsions (Linke & Drusch, 2017). The wettability is usually expressed by oil/water three-phase contact angle ($\theta_{o/w}$). Colloidal particles with equilibrium $\theta_{o/w}$ at oil/water interface could promote effective packing of particles and form a steric barrier, thus preventing the droplet coalescence (Gao et al., 2014). In order to form stable Pickering emulsions, some feasible methods were utilized to regulate the surface wettability of zein particles. Gao et al. (2014) reported that zein and sodium stearate (SS) complexes, which formed through nonspecific hydrophobic interaction, significantly improved the diffusive mobility and equilibrated interfacial wetting properties of particles. Thus the interfacial particle was strongly favored adsorption and evidently enhanced the stability of Pickering emulsions against coalescence and creaming. However, the safety problems of SS were limited their application in food industries. Therefore, natural renewable resources (proteins and polysaccharides) were alternatively utilized to form complex particles with zein, tuning the three-phase contact angle of zein colloidal nanoparticles. Feng & Lee (2016) reported that sodium caseinate (NaCas) could adsorb onto zein colloidal nanoparticles and adjust the oil-in-water three phase contact angle $\theta_{o/w}$ close to 90°. In comparision with zein emulsions, the zein/NaCas nanocomplexes stabilized Pickering emulsions exhibited a better centrifugal stability at most pH values and ionic strengths. Highly charged zein/chitosan colloid particles (ZCCPs) with an intermediate wettability produced by a facile anti-solvent procedure were shown to be effective Pickering emulsifiers (Wang et al., 2015, 2016). Soltani and Madadlou (2016) also showed that sugar beet pectin and zein complex particles significantly improved the stability of Pickering emulsions, which was attributed to enhanced steric and electrostatic repulsion.

Gum arabic (GA), an amphiphilic polysaccharide, is widely utilized in the food industry because of its persistent stability in a wide pH range, high ionic strength, and high temperature (Bai, Huan, Li, & McClements, 2017; Chen & Zhong, 2015). Chen and Zhong (2015) presented that GA adsorbed on zein nanoparticles to stabilize nanoparticles in a wide pH range through electrostatic and hydrophobic interactions. To date, there has been no a systematic study on zein and GA complex colloidal particles as Pickering emulsion stabilizers. Interestingly, transforming Pickering emulsions to emulsion gels becoming an emerging trend. Pickering emulsion gels which possessed a gel-like network, endowed them superior stabilization (oxidative and physical stability) and better delivery for bioactives (Liu & Tang, 2016a, b; Hoffmann & Reger, 2014).

The purpose of this study was to form a novel, long-term stable, surfactant-free, and edible Pickering emulsion gels. Therefore, zein and GA complex colloidal nanoparticles ($ZGAP_S$) were fabricated by anti-solvent precipitation method as novel renewable natural particle-stabilizers of Pickering emulsion gels. The physical (particle size) and surface properties (wettability and surface charge) of complex colloidal particles were investigated. Fourier transform infrared spectroscopy (FTIR) was used to identify the driving forces for the formation of complex colloidal nanoparticles. Furthermore, the Pickering emulsion gels were characterized using particle size, confocal laser scanning microscopy (CLSM), optical microscopy and rheological measurements. The influence of oil phase ratio on the properties of Pickering emulsion gels were investigated. Moreover, the stability of Pickering emulsion gels against environmental stresses including pH and heat were also discussed. The information from this study would provide a new method for developing zein-based Pickering emulsion gels, which could be used as a novel carrier of bioactive components.

2. Materials and methods

2.1. Materials

Zein (product Z3625) and fluorescent dyes (Nile Red and Nile Blue A) were purchased from Sigma-Aldrich (St. Louis, MO, USA). GA was obtained from Shanghai Intron Food Co., Ltd. Medium chain triglyceride (MCT) oil was acquired from Lonza Inc. (Allendale, NJ, USA). All other chemical agents were analytical grade.

2.2. Fabrication of zein and GA complex colloidal nanoparticles ($ZGAP_S$)

Zein colloidal nanoparticles were prepared by anti-solvent precipitation method. Briefly, 4.0 g zein was dissolved in 100 mL 70% (v/v) aqueous ethanol solution with magnetic stirring to form stock solution. Then the stock solution was added drop-wise into 300 mL deionized water under continued stirring (600 rpm). After 30 min of constant stirring, the remained ethanol in the particle dispersions was removed by rotary evaporator (45 °C). Finally, the concentration of zein in the particle dispersions was 2% (w/v). The pH of zein particle dispersions was adjusted to 4.0 using 0.1 N HCl or NaOH.

Different concentrations of GA solutions were prepared by dissolving GA in deionized water and stirring overnight. After dissolution, GA solutions were adjusted to pH 4.0 using 0.1 N HCl or NaOH. Then zein particle dispersions (2%, w/v) were added to the different concentrations of GA solutions. The ZGAPs dispersions were formed with zein to GA mass ratios of 5:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:5 (w/w) and termed as ZGAPs5:1, ZGAPs3:1, ZGAPs2:1, ZGAPs1:1, ZGAPs1:2, ZGAPs 1:3 and ZGAPs1:5. The ZGAPs dispersions were store at 4 °C for further analysis. Some parts of samples were lyophilized for 48 h (Alpha 1-2 D Plus freeze-drying apparatus, Marin Christ, Germany).

2.3. Particle size, zeta (ζ)-potential and polydispersity index (PDI) of ZGAPs

Dynamic light scattering (DLS) and particle electrophoresis instrument (Zetasizer Nano-ZS90, Malvern Instruments Ltd., Worcestershire, UK) were used to determine the particle size, ζ-potential and PDI of particle dispersions according to the method in our previous report (Dai, Sun, Wang, & Gao, 2016). Samples were diluted to the appropriate concentration before detecting. All measurements were carried out at 25 °C.

2.4. Wettability measurement of ZGAPs

The three-phase contact angle ($\theta_{o/w}$) of particles (zein, GA and