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Formation and characterization of zein-propylene glycol alginate-surfactant ternary complexes: Effect of surfactant type

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ABSTRACT

In this study, zein, propylene glycol alginate (PGA) and surfactant ternary complexes were fabricated by anti-solvent co-precipitation method. Two types of surfactants (rhamnolipid and lecithin) were applied to generate zein-PGA-rhamnolipid (Z-P-R) and zein-PGA-lecithin (Z-P-L) ternary complexes, respectively. Results showed that the surfactant types significantly affected the properties of ternary complexes. The formation of ternary complexes was mainly due to the non-covalent interactions such as hydrogen bonding, electrostatic interaction and hydrophobic interactions among zein, PGA and surfactants. Moreover, the thermal stability of ternary complexes was enhanced with increasing the levels of both surfactants. Notably, ternary complex dispersions exhibited better stability against pH from 2 to 8. Furthermore, a compact network structure was observed in Z-P-R ternary complex, while Z-P-L ternary complex remained the spherical structure. These findings would provide new insights into the development of novel delivery system and expand the options, when zein-based complexes were utilized under different environment conditions.

1. Introduction

Zein, a prolamine protein from corn, has recently received an increasing attention from researchers, due to its unique solubility property, environment-friendly, biocompatibility, biodegradability and GRAS (generally recognized as safe) (Chang, Wang, Hu, & Luo, 2017a, 2017b; Chang, Wang, Hu, Zhou, et al., 2017; Shukla & Cheryan, 2001). Because of its more than 50% non-polar amino acids, zein is water-insoluble but can be well dissolved in 50–90% aqueous ethanol or strong alkali solutions (pH > 11) (Pan & Zhong, 2016; Sun, Dai, & Gao, 2016). Due to its inherent hydrophobic property, zein nanoparticles can be easily formed through liquid-liquid dispersion method, which is also regarded as anti-solvent precipitation (ASP) (Chang, Wang, Hu, & Luo, 2017a, 2017b; Dai, Sun, Li, et al., 2017). Thus, zein nanoparticles were widely used as delivery systems for hydrophobic bioactive compounds such as quercetagetin (Q) (Sun et al., 2016), curcumin (Chang, Wang, Hu, & Luo, 2017a, 2017b; Chang, Wang, Hu, Zhou, et al., 2017; Dai, Sun, Wei, Mao, & Gao, 2017; Hu et al., 2015; Patel, Hu, Tiwari, & Velikov, 2010), lutein (Chuacharoen & Sabliov, 2016), β-carotene (Wei, Sun, Dai, Zhan, & Gao, 2018) and α-tocopherol (Luo, Zhang, Whent, Yu, & Wang, 2011).

Although zein nanoparticles have many advantages, the application of zein nanoparticles is limited due to it's sensitive to enzymatic degradation and easily aggregated during storage (Pan, & Zhong, 2016; Patel, Bouwens, & Velikov, 2010). In order to improve the stability and expand the application of zein nanoparticles, zein-caseinate (Chen & Zhong, 2014; Patel, Hu, et al., 2010; Patel, Bouwens, et al., 2010), zein-polysaccharide (Dai, Sun, Wei, et al., 2017; Hu & McClements, 2015; Hu et al., 2015; Wang et al., 2015) and zein-surfactant (Chuacharoen & Sabliov, 2016; Hu & McClements, 2014) binary complex nanoparticles with a core-shell structure were prepared by ASP, by which zein ethanol solution was dropwised into caseinate/polysaccharide/surfactant aqueous solution under stirring. Nevertheless, the aforementioned polysaccharides were mainly referred to hydrophilic biopolymers, including chitosan (Wang et al., 2015), gum arabic (Dai, Sun, Wei, et al., 2017), pectin (Hu et al., 2015) and sodium alginates (Hu & McClements, 2015). Interestingly, in our preliminary experiment, we successfully fabricated zein-propylene glycol alginate (PGA) binary complex nanoparticles through the method of anti-solvent co-precipitation (ASCP), which was different from ASP (Sun et al., 2016). The ASCP meant that both zein and PGA were dissolved in aqueous ethanol solution and then dropped into distilled water under mild stirring. The presence of PGA significantly improved thermal stability, entrapment efficiency and loading capacity of zein nanoparticles (Sun et al., 2016).

PGA, a high molecular weight linear polysaccharide with 50–85% of the esterified carboxyl groups, is derived from the reaction between

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propylene oxide and alginic acid (Chen, Chen, & Hsieh, 2016; Martinez, Ruiz-Henestrosa, Sánchez, Patino, & Pilosof, 2012). Additionally, PGA is composed of 31–65% 1,4 linked-D-mannuronic acid and 69–35% L-guluronic acid and always used as stabilizers and foaming agents (Baeza, Pilosof, Sanchez, & Rodríguez Patino, 2006; Sarker & Wilde, 1999). Hadef, Rogé, and Edwards-Lévy (2015) reported that human serum albumin (HSA) and ester groups of PGA could form the amide bonds in the inner aqueous phase after alkalization. Zein and PGA binary complex nanoparticles were formed through hydrogen bonding and hydrophobic interactions (Sun et al., 2016). Although zein-polysaccharide binary complex nanoparticles showed the desirable stability, zein/caseinate/pectin ternary complex nanoparticles exhibited better properties such as stabilization effect under simulated gastrointestinal conditions (Chang, Wang, Hu, & Luo, 2017a, 2017b; Chang, Wang, Hu, Zhou, et al., 2017).

Lecithin, a natural small molecular surfactant, which is composed of a glycerol backbone esterified with fatty acids and a phosphate group, has amphiphilic property and is extensively used to reduce the interfacial tension and improve the stability of emulsions (Dai, Sun, Wang, & Gao, 2016; Sui et al., 2017). Normally, the application of small molecule surfactant in food systems (emulsion or ice cream) is usually combined with proteins. Hence, the interactions between lecithin and water-soluble proteins have attracted extensive attentions. Wang et al. (2017) reported that the combination of lecithin and whey protein isolate (WPI) showed a synergistic effect on interface and endowed good characteristics to emulsions. The presence of lecithin could change the surface activity of soybean protein (Sui et al., 2017). Notably, in our previous study, interactions between lecithin and water-insoluble protein (zein) in aqueous ethanol solution were investigated. Zein and lecithin composite colloidal nanoparticles prepared by ASCP were found to improve the functionality and stability of zein (Dai, et al., 2016; Dai, Sun, Li, et al., 2017).

Rhamnolipid, a bio-degradable biosurfactant produced by bacteria (like *Pseudomonas aeruginosa*), has a potential commercial application to form stable oil in water (o/w) emulsions (Nitschke, Costa, & Contiero, 2010). The structure of rhamnolipid is comprised of one or two polar rhamnose units and one non-polar fatty acid chain, which gives the rhamnolipid active surface. Because of its carboxylic acid group, rhamnolipid has a negative charge at appropriate pH range (Helvacı, Peker, & Özdemir, 2004; Nitschke et al., 2010). Bai and McClements (2016) reported that rhamnolipid-coated o/w emulsion droplets showed a high negative charge at neutral pH. As mentioned above, small molecule surfactant and protein coexisted in food system and the interactions between them were of crucial importance to food quality. However, there were few studies about the effect of rhamnolipid on the properties of proteins.

Therefore, in this work, zein/polysaccharide/surfactant ternary complexes were fabricated by ASCP. A hypothesis was proposed that ternary complexes might have a new structure and improve the stability of zein nanoparticles. Additionally, two types of small surfactants, including rhamnolipid and lecithin, were used in the formulation. The different types and concentrations of surfactants on the physical properties such as particle size and zeta potential of ternary complexes were investigated. The Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to evaluate the interactions among zein, PGA and surfactants. The changed conformation of zein was investigated by fluorescent spectroscopy. The stability of ternary complexes against pH and ionic strength were also evaluated. Furthermore, the morphological structure and thermal stability were determined by scanning electron microscope (SEM) and differential scanning calorimetry (DSC), respectively.

2. Materials and methods

2.1. Materials

Zein (91.3% of protein content, w/w) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Food grade PGA (87.9% esterified carboxyl groups) was kindly provided by Hanjun Sugar Industry Co. Ltd. (Shanghai, China). Rhamnolipid (> 90% purity) was from Shaanxi Parnell Biological Technology Co. Ltd (Shaanxi, China). Soy lecithin (S-100) with a phosphatidylcholine content of 94% was purchased from Lipoid (Ludwigshafen, Germany). Absolute ethanol was acquired from Lanyi Chemical Products Co., Ltd. (Beijing, China). All other chemical reagents (sodium hydroxide and hydrochloric acid) used in this work were of analytical grade.

2.2. Fabrication of ternary complexes

Zein-PGA-rhamnolipid and zein-PGA-lecithin ternary complexes were prepared by ASCP according to the method of Dai, Sun, Li, et al. (2017) with some modifications. Briefly, zein (1.0 g) and PGA (0.2 g) were firstly dissolved in 100 mL 70% aqueous ethanol solution (v/v). Then certain amount of rhamnolipid with different mass ratios of zein to rhamnolipid (10:1, 5:1, 2:1, 1:1 and 1:2, w/w) were added into zein-PGA mixed aqueous ethanol solution. Afterwards, zein-PGA-rhamnolipid solutions were stirred at 600 rpm for 2 h (25 °C). Then, 20 mL zein-PGA-rhamnolipid stock solution was injected into a glass beaker with 60 mL distilled water to form ternary complex. The ternary complex dispersion was gently stirred for extra 30 min at room temperature. The ethanol remained in the dispersion was removed by a vacuum rotary evaporator at 45 °C and the pH of final dispersion was adjusted to 4.0 by 0.1 mol/L hydrochloric acid or sodium hydroxide solution. Finally, the concentration of zein in the dispersion was 0.25% (w/v). Additionally, part of ternary complex dispersion was stored in the refrigerator at 4 °C before used. And other part was freeze-dried to obtain powder of ternary complex for further analysis. Besides, zein, zein-PGA, and zein-PGA-lecithin ternary complex were also obtained by the aforementioned method. In this study, samples of zein-PGA-rhamnolipid ternary complex with different mass ratios of zein to rhamnolipid (1:0, 10:1, 5:1, 2:1, 1:1, 1:2) were termed as Z-P, Z-P-$R_{10:1}$, Z-P-$R_{5:1}$, Z-P-$R_{2:1}$, Z-P-$R_{1:1}$ and Z-P-$R_{1:2}$, respectively. Similarly, samples of zein-PGA-lecithin ternary complex with different mass ratios of zein to lecithin (10:1, 5:1, 2:1, 1:1, 1:2) were named as Z-P-$L_{10:1}$, Z-P-$L_{5:1}$, Z-P-$L_{2:1}$, Z-P-$L_{1:1}$ and Z-P-$L_{1:2}$.

2.3. Measurements of particle size and zeta potential

The particle size and zeta-potential (ζ-potential) of freshly prepared zein, Z-P, Z-P-R and Z-P-L ternary complex dispersions were measured by dynamic light scattering (DLS) using a Zetasizer Nano-ZS90 (Malvern Instruments, Worcestershire, UK) at 25 °C. The particle size was calculated using the Stokes-Einstein equation. The zeta-potential of the particles was obtained using the Smoluchowski model through electrophoretic mobility measurements performed in a capillary electrophoresis device inserted into the DLS instrument. The samples were diluted to an appropriate concentration before measurement to avoid the effects of multiple scattering. All measurements were performed in triplicate.

2.4. Fluorescence spectroscopy

The intrinsic fluorescence of samples was measured by a fluorescence spectrophotometer (F-7000, Hitachi, Japan). Briefly, samples were diluted to a constant concentration with 0.2 mg/mL zein and put into a cuvette. The fluorescence spectra of samples were collected by scanning at excitation wavelength 280 nm. Additionally, the emission wavelength was set from 290 to 450 nm. All data were collected at