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Effect of xanthan gum on walnut protein/xanthan gum mixtures, interfacial adsorption, and emulsion properties

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ABSTRACT

Effect of xanthan gum (XG) on the walnut protein/xanthan gum mixtures (WP/XG, 1.2 wt% WP and 0–0.30 wt% XG), interfacial adsorption and emulsions properties was studied. As XG concentrations increased, the aqueous solutions of WP/XG mixtures were clear at pH 7.0 as shown by phase diagram, however, bigger hydrodynamic diameter (D_H) and lower negative ζ-potential were observed which might be resulted from the formation of the co-solubilized WP/XG mixtures induced by electrostatic and hydrophobic interactions. As adsorption time prolonged, interfacial pressure (π), dilatational modulus (E), and dilatational elasticity (E_d) continuously increased, diffusion rate (k_{diff}) firstly increased and then decreased, inversely, penetration rate (k_P), rearrangement rate (k_R), dilatational viscosity (E_v) and loss-angle tangent (tanθ) decreased. These results indicated that XG promoted WP molecules to be continuously adsorbed to oil-water interface and formed firmer elastic interfacial films, possibly due to lower thermodynamic compatibility or higher viscosity. The oil droplets in emulsions stabilized by WP/XG mixtures had larger $d_{4,3}$ and lower negative ζ-potential, and flocs were observed by CLSM images, which might be related to the adsorption of WP. Emulsions exhibited pseudo-plastic and shear-thinning properties by flow behavior measurements, and emulsions stability presented by creaming index (*CI*) was firstly decreased caused by flocs and then increased due to higher viscosity.

1. Introduction

Walnuts (*Juglans regia* L.) are widely distributed in the world and especially in China. All parts from the walnuts (leaves, barks, stems, pericarps, fruits, flowers and ligneus membranes, etc.) are applied in agricultural and pharmaceutical areas due to its high nutrition and economic values (Mao & Hua, 2014). Walnuts contain 65% oils and 18–24% proteins (Mexis, Badeka, Riganakos, Karakostas, & Kontominas, 2009). Walnut oil, which riched in monounsaturated and polyunsaturated fatty acids, is the major product of walnut (Ros et al., 2004). The defatted walnut meal, the by-product from the production and market in walnut oil, is usually used as forage, causing a huge waste. In fact, defatted walnut meal contains a large amount of walnut protein (WP). WP contains 18 types of amino acids, including eight types of essential amino acids needed by the human body (Wang, Chen, Li, Zhou, & Xu, 2016), which shows a series of nutrition and health care functions. At present, numerous researchers have explored the biological activities of WP and their hydrolysates, especially in the antioxidant activities (Chen, Yang, Sun, Niu, & Liu, 2012; Jahanbani et al., 2016; Liu et al., 2016; Mao & Hua, 2014; Wang et al., 2016). However, fewer researches were concentrated on the interfacial characteristics of the WP.

Proteins and polysaccharides usually coexist in food emulsions as essential functional ingredients, and the interactions between biopolymers have a great effect on the emulsions systems (Chityala, Khouryieh, Williams, & Conte, 2016; Dickinson, 2008; Khouryieh, Puli, Williams, & Aramouni, 2015). The protein with distinctive surface activity can be spontaneously adsorbed to the oil-water interface and used as emulsifiers in food and maquillage fields (Baeza, Carrera, Rodríguez Patino, & Pilosof, 2005). The polysaccharide is mainly used as thickening or stabilizing agents to retard the phase separation and gravity-induced creaming by

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controlling the rheology properties and network structures of continuous phase (Dickinson, 2003). Many studies, which have been carried out to explore the interactions between proteins (i.e. whey protein, sodium caseinate, rice glutelin, etc.) and polysaccharides (i.e. xanthan gum, carrageenan, pectin, carboxymethyl cellulose, dextran sulfate, etc.) in either aqueous solutions or emulsion systems, were mainly involved in the properties of biopolymer mixtures, or interfacial adsorption, or emulsions (Jensen, Rolin, & Ipsena, 2010; Jourdain, Leser, Schmitt, Michel, & Dickinson, 2008; Koupantsis & Kiosseoglou, 2009; Liu, Zhao, Liu, & Zhao, 2011; Long et al., 2013; Xu, Luo, Liu, & McClements, 2017; Zhao et al., 2015). Those results have shown that the interaction (*i.e.* electrostatic, hydrophobic, etc.) between biopolymers have great influence on their properties and application in different systems. Meanwhile, the interaction or properties of the biopolymers are affected by many factors, such as the type and dosage of the protein or polysaccharide, the ionic strength or pH value of aqueous solutions. So, the researches about mixtures containing protein and polysaccharide at interface are of great interest in the theoretical exploration and practical application in real food systems.

Xanthan gum (XG), a rigid linear polysaccharide with trisaccharide side-chains whose negative charge, has been widely used in food emulsions due to its specific rheological features, such as favorable pseudo-plastic and shear-thinning behavior, resulting in resisting the Brownian motion of oil droplets and keeping static stability of emulsions (Dario, Hortencio, Sierakowski, Neto, & Petri, 2011; Kobori, Matsumoto, & Sugiyama, 2009).

In our previous study, we have already found that the oil-water interfacial and emulsifying properties of WP/XG could be affected by NaCl (Tan et al., 2017). However, the properties of the aqueous WP/XG solutions and the emulsions stabilized by WP/XG might be greatly affected by XG concentrations dependant WP/XG interaction. So, the objectives of this study were to investigate the effect of XG on (i) the properties of WP/XG mixtures in aqueous solutions (i.e. phase diagram, ζ-potential, hydrodynamic diameter), (ii) the interfacial adsorption properties at oil-water interface (i.e. interfacial pressure, adsorption kinetics, interfacial dilatational viscoelastic properties), and (iii) the properties of emulsions stabilized by WP/XG mixtures (i.e. ζ-potential, droplet size, microstructure, surface protein content and concentrations, flow behavior, and creaming stability). Furthermore, the relationship between WP/XG interaction in aqueous solutions or oil-water interface and properties of WP/XG mixtures or emulsions was also revealed for the potential use of WP or WP/XG mixtures as functional ingredients in food systems.

2. Materials and methods

2.1. Materials

Walnut protein (WP) was made from defatted walnut meal through alkali extraction and acid precipitation in our laboratory with the following compositions: 87.90 wt% protein (N × 5.3), 4.62 wt% ash, 4.12 wt% moisture and 3.12 wt% fat. Xanthan gum (XG) for food grade with an average molecular weight of approximately 6 million was kindly provided by Deosen Ltd (Shandong, China). Commercial corn oil was purchased from local supermarket and purified with Florisil (60–100 mesh, Sigma Aldrich). Nile blue and Nile red were purchased from Sigma-Aldrich Chemical Ltd (St. Louis, USA). All other reagents were of analytical grade. Phosphate buffer solutions (PBS) (10 mM, pH 7.0 ± 0.1) were prepared with distilled water further purified with a Milli-Q filtration unit.

2.2. WP solutions, XG solutions, and WP/XG mixtures preparation

Stock solutions of 2.4 wt% WP and 1.0 wt% XG were prepared respectively by dissolving their powders in 10 mM PBS at pH 7.0, and then stirred at room temperature by moderate shear-rate until completely dissolved. The WP/XG mixtures, containing a final constant WP concentrations of 1.2 wt% and a different XG concentrations (0, 0.05, 0.10, 0.20 and 0.30 wt%), were firstly prepared by mixing the appropriate volume of stock solutions, and then stirred at room temperature for at least 1.5 h to the homogeneous mixing.

2.3. Emulsions preparation

The oil-in-water emulsions, containing 90 wt% WP/XG mixtures solutions and 10 wt% corn oil, were prepared firstly by a high speed homogenizer (Ultra-Turrax T25, Staufen, Germany) operated at 10,000 rpm for 1 min, and then immediately homogenized with a 2-stage single-piston homogenizer (APV-1000, Albertslund, Denmark) at 40 MPa for once, and 10% of total pressure was maintained over the second valve. Sodium azide (0.02 wt%) was added as an anti-microbiological agent. The emulsions were stored at 4 °C for further analysis. All tests were completed within 3–24 h.

2.4. WP/XG mixtures characterization

2.4.1. Phase diagram

The phase diagram of WP/XG mixtures was constructed at a final WP concentrations of 1.2 wt% and a XG concentrations ranging from 0 to 0.30 wt%. The pH was adjusted to values ranging from 8.0 to 2.5 using 1 M NaOH or 1 M HCl. WP/XG mixtures were stored at room temperature for 12 h. The state of solubility of the WP/XG mixtures was assessed by visual observation after 12 h of storage, which was described as clear solution, cloudy solution, little precipitate and precipitate. Sodium azide (0.02 wt%) was added as an anti-microbiological agent during storage.

2.4.2. ζ-potential measurements

The ζ-potential of WP/XG mixtures and the emulsions stabilized by WP/XG mixtures was automatically calculated by Malvern Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK) at 25 °C, which was based on the analysis of particle electrophoretic mobility measurements. The mixtures or emulsions were diluted 50 times with 10 mM PBS at the same pH as the testing sample before measurements.

2.4.3. Hydrodynamic diameter (D_H) measurements

The hydrodynamic diameter (D_H) of WP/XG mixtures was determined by Malvern Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK) with a He-Ne laser (wavelength of 633 nm) at 25 °C. The mixtures were diluted with 10 mM PBS until the WP concentrations reached to 0.10 wt%. The diluted sample (1.2 mL) was put in the cell and equilibrated for 1 min before analysis.

2.5. Interfacial adsorption characterization

The interfacial adsorption property of WP/XG mixtures at the oil-water interface was measured by an optical contact angle meter (OCA-20, Dataphysics Instruments GmbH, Germany) with oscillating drop accessory (ODG-20, Dataphysics Instruments GmbH, Germany), and was assessed by the interfacial pressure (π), adsorption kinetics and interfacial dilatational viscoelastic properties. The WP/XG mixtures were diluted 10 times with 10 mM PBS at pH 7.0 before measurements. All experiments were carried out at 25 °C.