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Effect of fish gelatine-sodium alginate interactions on foam formation and stability

Natthiya Phawaphuthanon[a,b], Daeung Yu[c], Peerapong Ngamnikom[a,c], Il-Shik Shin[a], Donghwa Chung[c,d,e,*]

[a] Department of Marine Food Science and Technology, Gangneung-Wonju National University, Gangneung, 25457, Republic of Korea
[b] Nine Tamarind Co., Ltd., Phetchaboon, 67000, Thailand
[c] Institute of Green Bio Science and Technology, Seoul National University, Pyeongchang, 25354, Republic of Korea
[d] Graduate School of International Agricultural Technology, Seoul National University, Pyeongchang, 25354, Republic of Korea
[e] Center for Food and Bioconvergence, Seoul National University, Seoul, 08826, Republic of Korea

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ABSTRACT

The effect of fish gelatine (FG) – alginate (AL) interactions on the formation and stability of foams was investigated by examining relationships between surface, bulk, and foaming properties of aqueous mixtures of FG and AL at 25 °C under different values of pH and FG:AL ratio. Replacing a portion of FG with AL (FG:AL ratio = 80:20, 50:50, and 20:80) at pH 5.0 or 7.0 increased the air-liquid surface tension, negative electrophoretic mobility, bulk viscosity, and particle size of FG – AL mixtures. At pH 3.5 (below the isoelectric point of FG), the AL replacement increased the particle size more dramatically; however, it suppressed trends of increasing negative electrophoretic mobility and bulk viscosity, and even reduced the surface tension, due to stronger electrostatic attractions between oppositely charged FG and AL molecules and the resulting formation of more charge-neutralised FG – AL complexes. Foaming ability became stronger as the surface tension decreased, the negative electrophoretic mobility approached to zero (more charge-neutralised), and the bulk viscosity decreased; however, it was not closely correlated with particle size. FG – AL mixtures had a weaker foaming ability than solutions prepared only with FG or whey protein concentrate; however, these mixtures exhibited much higher foam stability during storage at 25 °C. FG – AL mixtures prepared at pH 3.5 and a FG:AL ratio of 80:20 showed the best foaming ability and foam stability.

1. Introduction

Foams are a type of dispersed systems that consist of a gaseous phase dispersed in a continuous liquid or a solid phase. They are the basic component of a variety of food products including whipped cream, desserts, smoothies, mousses, marshmallow, meringues, and ice cream. Proteins such as egg white, soy, or whey protein are the most widely used macromolecular foaming agents in the food industry (Liszka-Skoczylas, Ptaszek, & Żmudziński, 2014; Miquelim, Lannes, & Mezzenga, 2010). Polysaccharides (such as xanthan gum, guar gum, and κ-carrageenan) are often used to improve the stability of protein-based foams. These materials improve foam stability by different mechanisms, including thickening effects, and interactions (attractive or repulsive) between proteins and polysaccharides (Dickinson, 2003; Liszka-Skoczylas et al., 2014; Miquelim et al., 2010; Narchi, Vial, & Djelveh, 2009).

Proteins may undergo either attractive or repulsive interactions with polysaccharides, depending on conditions within aqueous medium conditions (Razzak, Kim, & Chung, 2016; Yang, Anvari, Pan, & Chung, 2012). Attractive interactions are driven mostly by electrostatic interactions between positively charged proteins and negatively charged polysaccharides. These interactions induce the formation of either soluble or insoluble biopolymer complexes. Repulsive interactions are dominant when proteins and polysaccharides are uncharged or similarly charged, resulting in thermodynamic incompatibility between the two biopolymers (Harnsilawat, Pongsawatmanit, & McClements, 2006). These interactions form a two-phase system consisting of protein-rich and polysaccharide-rich phases at high biopolymer concentrations, but at dilute concentrations, the two biopolymers are cosoluble in a single phase. Previously, Miquelim et al. (2010) showed that the stability of egg albumin-based foam was enhanced by the addition of κ-carrageenan at a pH below the protein's isoelectric point due to attractive

* Corresponding author. Graduate School of International Agricultural Technology, Seoul National University, Pyeongchang, 25354, Republic of Korea.
E-mail address: dchung@snu.ac.kr (D. Chung).

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protein-polysaccharide interactions. Perez, Sánchez, Patino, Rubiolo, and Santiago (2010) reported that surface and viscoelastic properties of β-lactoglobulin or whey protein concentrate at the air-water interface were improved by the addition of xanthan gum; they attributed their results to repulsive protein-polysaccharide interactions that could induce thermodynamic incompatibility and segregative separation of the biopolymers.

Fish gelatine (FG) has been proposed as an alternative to mammalian gelatines as it dispels consumer concerns regarding both cultural/religious dietary restrictions and contamination with bovine spongiform encephalopathy, and can be easily obtained from by-products of the fishery industry (Karim & Bhat, 2009; Yang et al., 2012). FG has lower contents of proline and hydroxyproline (about 17–25% of total amino acids) than mammalian gelatines (about 30% of total amino acids) (Karim & Bhat, 2009). The hydroxyl group of proline and hydroxyproline can form hydrogen bonding with water molecules, and therefore, FG shows different physicochemical and functional properties, including weaker gelling properties, compared to mammalian gelatines due to less hydrogen bonding (Karim & Bhat, 2009). Previous studies showed that FG obtained from the skin of different fish species – including sole, squid, cuttlefish, unicorn leatherjacket, grey triggerfish, and channel catfish – exhibited comparable foaming properties to mammalian gelatines (Aewsiri, Benjakul, Visessanguan, Wierenga, & Gruppen, 2011; Ahmad & Benjakul, 2011; Duan, Zhang, Liu, Cui, & Regenstein, 2018; Giménez, Alemán, Montero, & Gómez-Guillén, 2009; Jellouli et al., 2011; Nagarajan, Benjakul, Prodpran, Songtipya, & Kishimura, 2012). However, the foaming properties of FG in the presence of polysaccharides have not been previously reported.

Alginate (AL) is a linear anionic polysaccharide that consists of 1,4-linked-α-L-guluronic acid and β-D-mannuronic acid groups. It is found mainly in brown seaweeds, and is widely used as a thickener, stabilizer, or gelling agent in foods, pharmaceuticals, and cosmetics preparations (Razzak et al., 2016). Razzak et al. (2016) demonstrated that AL interacts electrostatically with FG in aqueous media to form either solid-state insoluble complexes (i.e. precipitates) or soluble complexes depending on pH, the FG-to-AL weight ratio (FG:AL ratio), total biopolymer concentration, and ionic strength.

The objective of this study was to investigate the effect of FG − AL interactions on the formation and stability of foams. This was achieved by examining the relationship between the surface, bulk, and foaming properties of aqueous mixtures of FG and AL – including surface tension, electrophoretic mobility, viscosity, particle size, foam ratio (FR), and bubble size – under different values of pH and FG:AL ratio, which are known primary factors influencing interactions between FG and AL. For comparison purpose, the properties of whey protein concentrate (WPC), often used as a commercial foaming agent in food industry (Liszka-Skoczylas et al., 2014), were also examined.

2. Materials and methods

2.1. Materials

FG derived from the skin of cold-water fish (including cod, Pollock, and haddock; 80.2% protein, 8.7% carbohydrates, 0% lipid, 11.0% moisture, and 0.1% ash) and AL from brown algae (extra pure sodium salt; mannuronic acid to guluronic acid ratio = ~0.8; 3.4% protein, 60.8% carbohydrate, 0.5% lipid, 10.9% moisture, and 24.4% ash) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA) and Kanto Chemical Co., Inc. (Tokyo, Japan), respectively. Commercial whey protein concentrate (WPC; 65.7% protein, 24.5% carbohydrate, 1.4% lipid, 5.5% moisture, and 2.6% ash) was obtained from Hilmar Cheese Company, Inc. (Hilmar, CA, USA). The proximate compositions of the biopolymers were determined using Kjeldahl method for protein, phenol-sulfuric acid method for carbohydrate, Soxhlet method for lipid, and Karl-Fisher method for moisture. The weight average molar mass of FG (56 kDa), AL (233.4 kDa), and WPC (20.9 kDa) were measured by high performance size exclusion chromatography coupled to multiangle laser light scattering and refractive index detection system (HPSEC-MALLS-RI) according to the method of Yang, Chung, and You (2008) with slight modifications. Sodium azide (NaN_3) was obtained from Daehung Chemicals & Metals (Siheung, Korea).

2.2. Preparation of biopolymer mixtures

Aqueous solutions of FG and AL were prepared separately in a citrate-phosphate buffer at pH 3.5, 5.0, or 7.0 with 0.02% (w/v) of sodium azide as a preservative. These solutions were placed in a water bath and shaken at 100 rpm for 24 h at either 40 °C (FG) or 80 °C (AL) to ensure complete dissolution of the biopolymers. FG and AL solutions were then cooled to 25 °C and mixed to prepare several 50 mL FG − AL mixtures with a total biopolymer concentration of 0.5% (w/v) at different values of FG-to-AL weight ratio (FG:AL rato = 100:0, 80:20, 50:50, 20:80, and 0:100). The mixtures were stirred for 90 min to ensure sufficient biopolymer interactions, and stored at 25 °C for 24 h to reach equilibrium before experiments were performed. Aqueous solutions of WPC (0.5%, w/v) were also prepared separately at pH 3.5, 5.0, or 7.0 using the same method used to prepare FG solutions.

2.3. Measurement of biopolymer mixture properties

The surface tension (γ, mN/m) of the biopolymer solutions and mixtures at the air-liquid interface was measured at 25 °C via the Wilhelmy plate method using an automated force tensiometer (K100; Krüss GmbH, Hamburg, Germany). The electrophoretic mobility (μ, mm cm/V s) of biopolymers in the biopolymer solutions and mixtures was determined at 25 °C by laser Doppler electrophoresis combined with phase analysis light scattering (PALS) (Zetasizer Nano ZS; Malvern Instrument, Worcestershire, UK). The apparent viscosity (η, cP) of the biopolymer solutions and mixtures was determined using a rotational viscometer (LVDV–III Ultra; Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) equipped with SC4-18 spindle at 25 °C at a constant shear rate of 79.2 s^{-1} (60 rpm).

The volume-weighted mean diameter ($d_{4,3}$, nm) of biopolymers in the biopolymer solutions and mixtures was determined using dynamic light scattering. The fluctuation in scattered light intensity by the Brownian motion of biopolymers was detected at 25 °C using the Zetasizer. The intensity fluctuation was converted to a correlation coefficient, an expression for the time dependence of the fluctuation in scattered light intensity, and then to diffusion coefficient (D, m^2/s), followed by the calculation of hydrodynamic diameter (d_H, nm) using the Stoke-Einstein equation:

$$d_H(\times 10^6) = \frac{kT}{3\pi\eta D} \quad (1)$$

where k is the Boltzmann's constant (1.38×10^{-23} J/K), T is the absolute temperature (K), and η is the apparent viscosity (cP). The intensity-weighted distribution of d_H was generated and transformed to the volume-weighted distribution of d_H using the Mie theory to obtain the $d_{4,3}$ (Bhattacharjee, 2016; Stetefeld, McKenna, & Patel, 2016). Polydispersity index (PDI) was also obtained from the correlation coefficient using a cumulants analysis method. All data handling was carried out using the Zetasizer Nano software (Malvern Instrument, Worcestershire, UK).

2.4. Preparation of foams

Aqueous solutions of FG, AL, and WPC and aqueous FG − AL mixtures were prepared at 25 °C as described in Section 2.2. A volume of 50 mL of each biopolymer solution or mixture was transferred to a 100 mL cylinder and homogenized at 16,000 rpm for 2 min using an Ultra-Turrax T25 digital homogenizer (IKA, Staufen, Germany) to incorporate air.