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Processes improving the dispersibility of spray-dried zein nanoparticles using sodium caseinate

Huaiqiong Chen, Qixin Zhong*

Department of Food Science and Technology, The University of Tennessee, 2510 River Drive, Knoxville, TN 37996, USA

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ABSTRACT

Zein has been studied as a versatile food biopolymer to fabricate nanoparticles for encapsulating a large variety of bioactive compounds. Being water-insoluble prolamines, dispersing zein nanoparticles in aqueous systems is a challenge. Recently, sodium caseinate (NaCas) was observed to have improved the dispersibility of freeze-dried zein nanoparticles but not for spray-dried samples. In this paper, three different approaches were studied to produce spray-dried zein nanoparticles precipitated by dispersing aqueous ethanol solutions of zein into the aqueous phase. The control (S2) was produced by dispersing zein solution into NaCas dispersion without pH adjustment. The other two approaches involved conditions dissociating NaCas: adjusting NaCas dispersion to pH 11.0 (S5) or dissolving NaCas in heated zein solution before dispersing to a pH 8.0 buffer (S4). After hydrating the spray-dried powder, dispersions demonstrated varying turbidity and precipitation stability during storage. Entire NaCas was observed to have adsorbed on S2 zein nanoparticles, corresponding to bigger particles, higher turbidity and lower stability of dispersions than those of S4 and S5. Conversely, only κ-casein was on zein nanoparticles of S4 and S5, corresponding to a higher zein:casein mass ratio and higher surface hydrophobicity than that of S2. The best dispersibility was observed for S4 at pH 7.0 and 0–300 mM NaCl, with the smallest hydrodynamic diameter (~125 nm), lowest turbidity, and without precipitation during 15-day refrigerated storage. Compositional analyses suggested that κ-casein in S4 was a part of zein nanoparticle matrices and was not detached by increased ionic strength during storage. Conversely, caseins detached from zein nanoparticles of S2 and S5, causing particle aggregation and precipitation. Additionally, the approach in S4 utilized less ethanol (50% v/v vs. 80% in the other two approaches) to dissolve zein. Our work is significant in fabricating delivery systems of bioactive compounds utilizing zein as a carrier biopolymer.

1. Introduction

Recently, there have been increasing interests in utilizing food biopolymers to fabricate delivery systems of bioactive compounds because of their non-toxicity, biocompatibility and biodegradability (Chen, Remondetto, & Subirade, 2006). Some of these delivery systems have demonstrated sustained or targeted release of the encapsulated bioactive components (Benjamin, Silcock, Leus, & Everett, 2012; Muller et al., 2011; Xiao, Davidson, & Zhong, 2011a; Xiao, Davidson, & Zhong, 2011b). Zein is a group of alcohol-soluble protein (prolamines) extracted from maize (*zea mays*) kernel (Hu, Lin, Liu, Li, & Zhao, 2012) and has been studied as a carrier biopolymer to achieve gradual release of the encapsulated compound (Bobokalonov et al., 2012; Hu et al., 2012; Xiao et al., 2011b; Zhong & Jin, 2009a).

Zein is insoluble in water but is soluble in about 55–90% v/v aqueous ethanol (Zhong & Jin, 2009b). This solubility property has been studied in the liquid–liquid dispersion technique where an aqueous ethanol solution of zein is dispersed into water to precipitate zein to form nanoparticles (Zhong & Jin, 2009b). By co-dissolving in the aqueous ethanol solution, lipophilic bioactive compounds can co-precipitate with zein during liquid–liquid dispersion, which enables the encapsulation of a variety of bioactive compounds in nanocapsules to obtained gradual release (Wu, Luo, & Wang, 2012; Zhong & Jin, 2009a; Zhong, Tian, & Zivanovic, 2009). However, because zein has abundant non-polar amino acid residues such as leucine, proline, alanine and phenylalanine, the dispersibility of zein nanoparticles in aqueous systems is a challenge. Furthermore, zein is typically dissolved in 70–80% aqueous ethanol before preparation of nanoparticles using liquid–liquid dispersion (Zhong & Jin, 2009b), and it is desirable in the industrial production to reduce the usage of ethanol without compromising characteristics of zein nanoparticles. To favor

* Corresponding author. Tel.: +1 865 974 6196; fax: +1 865 974 7332.
E-mail addresses: qzhong@utk.edu, qzhong1@utk.edu (Q. Zhong).

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industrial applications, it is also desirable to prepare the powdered form of zein nanoparticles, preferably by spray-drying that is less expensive and more scalable than freeze drying (Desobry, Netto, & Labuza, 1997). Spray-dried powder also has more uniform particles and better flowability than that from freeze-drying, which favors the industrial production (Seville, Kellaway, & Birchall, 2002).

In a recent study, sodium caseinate (NaCas) was supplemented in water during liquid–liquid dispersion to stabilize zein nanoparticles, and the zein nanoparticles before and after freeze drying demonstrated much improved dispersibility and stability at pH 7.4 than the treatment without NaCas (Patel, Bouwens, & Velikov, 2010). This is a significant finding because the neutral acidity is nearby the isoelectric point (pI) of zein, around pH 6.2 (Patel et al., 2010). However, as detailed below, this approach was infeasible to disperse zein nanoparticles after spray drying.

We hypothesize that the application of dissociated NaCas in liquid–liquid dispersion can improve the dispersibility of spray-dried zein nanoparticles. NaCas is produced from fresh or pasteurized skim milk by precipitation near the pI of caseins (pH 4.6), followed by neutralizing the recovered precipitate using sodium hydroxide for spray drying (Neirynck, Van lent, Dewettinck, & Van der Meeren, 2007). NaCas is more soluble than casein micelles directly separated from bovine milk (Kalichevsky, Blanshard, & Tokarczuk, 1993) and is widely used in the food industry due to its versatile functional properties, such as emulsifying and stabilizing capacities (Corzo-Martinez, Moreno, Villamiel, & Harte, 2010). Like casein micelles, NaCas is composed of α_{s1}-, α_{s1}-, β-, and κ-caseins in weight proportions of approximately 4:1:4:1(Post, Arnold, Weiss, & Hinrichs, 2012). Because of the similarity in composition, conditions impacting casein micelle structures likely can be used to engineer the structure of NaCas. One such example is the dissociation of casein micelles in more than 30% ethanol at 60 °C, resulting in a translucent dispersion (O'Connell et al., 2003). The dissociated caseins can reform to nanoparticles at a reduced ethanol content and/or lowered temperature. Another example is the disruption of casein micelles when the pH is increased to 10.0, and the reformed casein particles after acidification back to pH 6.6 had a smaller particle size and a lower zeta-potential than the original casein micelles (Huppertz, Vaia, & Smiddy, 2010).

In this work, the major objective was to test the above hypothesis by incorporating the two conditions, i.e., hot aqueous ethanol and alkaline pH, in preparation of zein nanoparticles by liquid–liquid dispersion. Following spray drying, the obtained powder was re-dispersed in water and characterized for dispersibility and physicochemical properties important to dispersibility.

2. Materials and methods

2.1. Materials

Purified α-zein and ethanol (200 proof) were purchased from Acros Organics (Morris Plains, NJ). The NaCas was a product of Pfaltz & Bauer (Waterbury, CT). The α-, β-, and κ-caseins from bovine milk, with a purity of 70%, 98% and 70%, respectively, according to the product brochure, were procured from Sigma–Aldrich Corp. (St. Louis, MO). Potassium bromide (KBr) was a product from Fisher Scientific Inc. (Pittsburgh, Pa.)

2.2. Preparation of spray-dried zein nanoparticles

Ethanol concentration impacts zein nanoparticle properties produced by liquid–liquid dispersion (Zhong and Jin, 2009b) but was not studied in the present work. Three approaches were studied to fabricate zein nanoparticles, each at one ethanol concentration (Fig. 1). In Approach A, 2.0 g zein was dissolved in 100.0 mL of 80% v/v aqueous ethanol, followed by dispersing into 250.0 mL deionized water with or without 2.0 g sodium caseinate while being agitated at 10,000 rpm for 2 min by a high-speed homogenizer (model Cyclone I.Q.^{2}, The VirTis Company, Inc., Gardiner, NY). The dispersion was spray-dried using a bench-top spray dryer (model B-290, BÜCHI Corporation, Flawil, St. Gallen, Switzerland) with the parameters from the reference (Xiao et al., 2011b), which were a feed rate of 15%, an aspirator setting of 100%, and an inlet temperature of 105 °C. The samples were named as S1 for the treatment without NaCas and S2 for the one with NaCas. Preparation conditions of S1 and S2 were similar to those in the literature except the powdered sample was spray-dried instead of freeze-dried (Patel et al., 2010). In the approach B, 2.0 g zein and 0 or 2.0 g NaCas were mixed with 100.0 mL of 50% v/v aqueous ethanol containing 25 mM sodium phosphate. Following adjustment of pH to 8.0 and incubating in a 90 °C water bath for 30 min, the hot solution was dispersed into 400.0 mL of 25 mM sodium phosphate buffer previously adjusted to pH 8.0, followed by spray drying. The obtained samples were named as S3 and S4 for the treatment without or with NaCas, respectively. Sample S5 was prepared using approach C that was similar to approach A with NaCas, except that the aqueous NaCas dispersion was adjusted to pH 11.0 before dispersing the zein solution. The dispersion was adjusted back to pH 8.0 and spray-dried. Additionally, three samples containing NaCas only without zein were prepared through the three approaches A, B, and C, which were named as N1, N2 and N3,

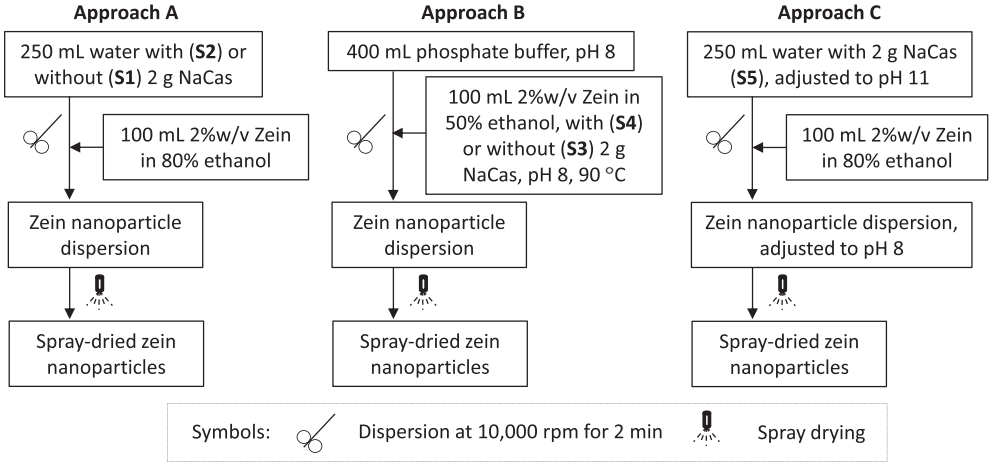

Fig. 1. Processes of producing spray-dried nanoparticles using approaches A, B, and C.