LWT - Food Science and Technology 68 (2016) 589–594

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Enhancing dispersion stability of alpha-tocopherol in aqueous media using maize starch and ultrasonication

Chuqiao Ren [a], Eun Young Park [a], Jong-Yea Kim [b, **], Seung-Taik Lim [a, *]

[a] School of Life Sciences and Biotechnology, Korea University, 5-1, Anam-dong, Sungbuk-ku, Seoul 136-701, South Korea
[b] Department of Food Science and Biotechnology, Kangwon National University, Chuncheon 200-701, South Korea

ARTICLE INFO

Article history:
Received 27 July 2015
Received in revised form
28 December 2015
Accepted 4 January 2016
Available online 6 January 2016

Keywords:
Alpha-tocopherol
Maize starch
Ultrasonication
Aqueous dispersion

ABSTRACT

Alpha-tocopherol (30–120 mg) was dispersed in an aqueous maize starch solution (0–240 mg starch solids in 30 mL) at various temperatures (60–80 °C) for 3 h, followed by cooling to 30 °C for different periods (0–12 h). The dispersion prepared under an optimized condition was subjected to ultrasonic treatment (up to 5 min in ice bath) to enhance the dispersion stability. When an aqueous α-tocopherol (60 mg) dispersion in a starch solution (120 mg in 30 mL) was prepared at 70 °C with cooling for 3 h and ultrasonic treatment for 3 min, a homogenous and opaque dispersion was obtained with 74% (w/w) of the α-tocopherol added was stably dispersed. The ultrasonic treatment decreased hydrodynamic diameter (from 1253 to 416 nm) and zeta-potential (from −6.28 to −22.40 mV) of the dispersed α-tocopherol particles, improving the dispersion stability. During a storage for 28 days at room temperature, the dispersion remained stable without producing any precipitates or aggregates. When the α-tocopherol dispersion in starch solution was subjected to autoclave treatment (121 °C for 20 min), 25% of the α-tocopherol in the dispersion was transformed to immiscible phase and phase-separated.

1. Introduction

Vitamin E, a well-known lipophilic natural antioxidant, is a widely used as an additive in foods, cosmetics and pharmaceuticals (Constantinides, Han, & Davis, 2006). It has physiological benefits, e.g., preventing oxidative damage and lipid peroxidation in the central and peripheral nervous systems (Scholz et al., 1997; Teranishi, Nakashima, & Wakabayashi, 2001; Terrasa, Guajardo, Marra, & Zapata, 2009). Tocols and tocotrienol derivatives exhibit an activity of vitamin E (Traber & Sies, 1996), but vitamin E is often referred to as α-tocopherol given which is predominant in nature with the highest biological activity (Brigelius-Flohé & Traber, 1999; Cheong, Tan, Man, & Misran, 2008).

Intestinal absorption of α-tocopherol requires the formation of micelles that contain dietary lipids and emulsification in the presence of bile slats, so the bioavailability of α-tocopherol is affected by food consumption, lipid digestion, and the formation of micelles (Hatanaka et al., 2010; Lodge, Hall, Jeanes, & Proteggente, 2004). The water-immiscibility of α-tocopherol, however, results in low bioavailability and limits its use in beverage products (Chen & Wagner, 2004). Recently, great attention has been drawn to functional beverages, and thus a demand for the use of vitamin E in beverages has increased. Emulsification is a common approach to overcome this problem associated with α-tocopherol use in food industry (Chen & Wagner, 2004; Cheong et al., 2008; Hatanaka et al., 2010). Thermodynamically metastable emulsion systems require emulsifying agents such as surfactant molecules (e.g., polysorbates) (Rousseau, 2000). Emulsifying agents for food and cosmetic applications are considered safe, but developing alternative approaches has been carried out to meet the consumer's demand for “clean label” products (Patel & Velikov, 2011; Wilcock, Pun, Khanona, & Aung, 2004).

Hydrocolloids and proteins may stabilize emulsion systems and are commonly used to control their stability (Dickinson, 2009). Under favorable conditions, proteins tend to be more efficient than hydrocolloids in the utilization as emulsifying agents because proteins generally have some affinity to hydrophobic compounds with surface activity (Dickinson, 2009). Protein-based emulsions, however, are susceptible to the destabilization under unfavorable

* Corresponding author.
** Corresponding author.
E-mail addresses: jongkim@kangwon.ac.kr (J.-Y. Kim), limst@korea.ac.kr (S.-T. Lim).

http://dx.doi.org/10.1016/j.lwt.2016.01.001
0023-6438/

environmental conditions. For example, casein-based emulsions are readily destabilized by acidification and calcium addition, and whey protein-based emulsions are unstable under thermal treatment (Dickinson, 2006, 2009; Dickinson & Parkinson, 2004). On the other hand, hydrocolloid-based emulsions containing gum arabic or modified starch are mostly stable over a wide range of physical conditions, such as thermal shock treatment and the addition of calcium salts (Chanamai & McClements, 2002). Considering the environmental conditions associated with typical beverage production (i.e., generally acidic conditions and thermal treatment for pasteurization), hydrocolloids are more suitable as the primary emulsion stabilizer for functional beverages (Dickinson, 2009). As structuring, thickening, and/or gelling agents in aqueous media or oil-in-water emulsions, many hydrocolloids may modify the rheology of the media or emulsions in which biopolymer network contributes in immobilizing the dispersed particles or droplets (Dickinson, 2009).

Starch is a low-cost, renewable, non-toxic hydrocolloid with wide uses in the food industry as a thickening and/or gelling agent in its native and modified forms. Aside from its major applications, starch may also be utilized as a stabilizer in dispersions and emulsions. As an example, octenylsuccinic starch could be used to stabilize vitamin E in aqueous dispersions (Chen & Wagner, 2004; Qiu, Yang, & Shi, 2015). However, no study has been carried out in the stabilization of vitamin E in aqueous media using native starch. In this study, the effects of starch addition and post-ultrasonication on the stability of α-tocopherol dispersed in aqueous solution were investigated.

2. Materials and methods

2.1. Materials

Normal maize starch was provided by Samyang Genex Company (Seoul, Korea) and α-tocopherol (purity > 95.5%) was purchased from Sigma Aldrich Company (St. Louis, MO, USA). All other chemicals used were of analytical grade.

2.2. Preparation of α-tocopherol dispersions

The aqueous α-tocopeherol dispersions (30 g total) were prepared under different conditions: 30–120 mg α-tocopherol, 60–240 mg starch (dry solids), reaction temperatures between 60 and 80 °C, dispersing times of 0, 1, 2, or 3 h, and cooling periods during 0, 3, 7 or 12 h. The α-tocopherol solids were pre-dissolved in absolute EtOH (10 mL). Normal maize starch dispersions were prepared by autoclaving at 121 °C for 20 min with purged N_2 gas for complete gelatinization of starch granules. The pre-dissolved α-tocopherol solutions was quickly poured into the starch solutions while vigorously stirring at 70 °C. The dispersions were then immediately evaporated (N-1100 rotary evaporator, EYELA, Tokyo, Japan) at 60 °C until the final volume reached approximately 30 mL to remove most of the ethanol. The treated dispersions were stirred in a water bath (SWB-10L-2, Major Science, Saratoga, CA, USA) at different temperatures (60–80 °C) and times (0–3 h) at a constant speed (1500 rpm). After the stirring, the dispersions were subsequently cooled to 30 °C in the water bath while stirring for different periods (0–12 h). To improve the stability of α-tocopherol dispersed in aqueous starch solutions, ultrasonic treatment (frequency 20 kHz, amplitude 20%, output power 350 W) in an ice bath for different periods (0–5 min) using an ultrasonic processor (Branson Sonifier-450, Emerson Industrial Automation, St. Louis, MO, USA). The dispersions were centrifuged (10,000 × *g* for 30 min at 30 °C), and then any precipitates and flocculants were removed. The homogeneous supernatant was tightly sealed and kept in a dark place before analyses. Control dispersions without tocopherol or starch were prepared according to the same procedure.

2.3. Tocopherol content

The α-tocopherol content in the dispersions was assessed using a high performance liquid chromatography (HPLC; Prostar 240, Varian medical systems, Palo Alto, CA) with a C-18 column (Shiseido, 4.6 × 150 mm, 5 μm, 120 Å) and monitored with a UV detector at 295 nm (Prostar 320 UV–VIS detector, Varian medical systems, Palo Alto, CA). Methanol was used as the mobile phase with flow rate at 1.2 mL/min, and injection volume was 50 μL. An aliquot of α-tocopherol dispersion (1 mL) was poured into an absolute EtOH (20 mL), and the mixture was vigorously stirred for 10 min to extract α-tocopherol and precipitate starch. After centrifugation (2280 × *g* for 15 min at 4 °C), the starch precipitate was removed and then the remained supernatant was filtered through a 0.50 μm hydrophobic syringe filter (Advantec MFS, Inc., Dublin, CA) prior to injection to the HPLC system. α-Tocopherol was also dissolved in EtOH (0.02–0.1 mg/mL) to prepare standard solutions. Standard curve (concentration verses peak area) was calculated by linear regression analysis to determine concentration of α-tocopherol in the samples. Recovery of α-tocopherol was calculated according to the equation below:

$$\text{Recovery of } \alpha-\text{tocopherol} = \frac{\text{Weight of } \alpha-\text{tocopherol in the dispersion}}{\text{Weight of added } \alpha-\text{tocopherol into reaction system}} \times 100$$

2.4. Particle size analysis

The hydrodynamic mean diameter of the particles in the dispersions was determined with a dynamic light scattering detector (Dynapro Titan, Wyatt Technology, Santa Barbara, CA) using a Dynamics program (Version 6.9.2.9, Wyatt Technology, Santa Barbara, CA). The viscosity and refractive index of the water at 20 °C, determined using calculation software, were 1.00 cP and 1.333, respectively.

2.5. Zeta potential analysis

The zeta potential value of the starch-tocopherol dispersions was measured using a Zeta-sizer (3000HS Advance Malvern Instruments Ltd., Worcestershire, UK). The measurements were carried out at an ambient temperature and pH 5.5.

2.6. Storage stability of dispersions

During the storage of the starch-tocopherol dispersions at an ambient temperature and in a dark place, an aliquot of the dispersion (1 mL) was taken. The hydrodynamic diameter and