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Spray drying of high hydrophilic solids emulsions with layered interface and trehalose-maltodextrin as glass formers for carotenoids stabilization

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ABSTRACT

Objectives of the present study were to spray dry high total solids content single layer (SL) and layer-by-layer (LBL) emulsions, and to compare the ability of the SL and LBL powders in preventing the loss of carotenoids upon storage in the vicinity of the glass transition temperature (T_g). Carotenoids stability in humidified spray dried (HSD), non-humidified freeze-dried (NHFD), and humidified freeze-dried (HFD) systems were determined as well. The loss of carotenoids followed first order loss kinetics. An initial rapid followed by a second slower first order loss kinetics was observed in the non-humidified spray dried (NHSD) systems. Storage of systems above the T_g delayed carotenoids losses based on the rate constants. The loss of carotenoids in LBL systems was more heat sensitive as the activation energies were generally higher. Activation energy decreased above T_g indicating that the loss of carotenoids became less temperature dependent. The application of LBL interface structure reduced the rate of carotenoids losses and can be applied to prevent loss of oil soluble bioactives in formulated materials.

1. Introduction

Bioactive compounds in food materials play an important role in the prevention of chronic and degenerative diseases in humans (van Dokkum et al., 2008). Carotenoids are generally present in fruits and vegetables. β-carotene is a highly lipophilic hydrocarbon that is present in its non-crystalline or crystalline form in foods. Among the provitamin A carotenoids, β-carotene possessed the highest vitamin A activity as well as the highest rate of conversion to vitamin A (Grune et al., 2010). Besides that, β-carotene also showed antioxidant activity and anticancer properties, and it may protect against heart disease (Bendich and Olson, 1989; Omenn et al., 1996; Albanes, 1999). However, isomerisation (Sweeney and Marsh, 1971) and oxidation (Simpson, 1985) may lead to the degradation of β-carotene. On the other hand, lutein is known as a xanthophyll due to the presence of hydroxyl groups in its molecular structure. Lutein was found to be able to prevent macular degeneration and cataracts (Kachik et al., 1997) as well as play a role in minimizing light-induced skin damage (Ribaya-Mercado and Blumberg, 2004). Dhuique-Mayer et al. (2007) found that xanthophyll had faster degradation rates than carotenes and lower heat stability. However, carotenoids have low bioavailability when present as crystals or within protein complexes in fruits and vegetables. This causes difficulty in the adsorption of carotenoids during digestion in the gastrointestinal tract (Williams et al., 1998). Bioavailability of carotenoids can be enhanced by using delivery with edible oil as oil improves carotenoids adsorption (van Het Hof et al., 2000).

Carotenoids can be dissolved and incorporated into the lipid phase of an oil-in-water (O/W) emulsion to improve its bioavailability. This will be followed by emulsifying of the oil phase with an aqueous phase containing an emulsifier. The emulsion can be dehydrated to obtain a continuous phase of the dried formulation using a glass-forming hydrophilic component (Drusch et al., 2006; Ramoneda et al., 2011; Spada et al., 2012). Several studies have shown that layer-by-layer (LBL) emulsion with layered interface structures have a higher stability towards environmental stresses such as heat treatment, variations in pH, freeze-thaw cycles, lipid oxidation and ionic strength (Ogawa et al., 2003; Aoki et al., 2005; Güzey and McClements, 2006; Gharsallaoui et al., 2010; Lim et al., 2014) which will result in an improved protection against degradation of the encapsulated bioactive compounds. The thicker interfacial layer too can increase the oxidative stability of LBL

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system as well as providing the particles with a higher stability towards disruptions (McClements, 1999; Klinkesorn et al., 2005). LBL emulsion can be obtained via electrostatic attraction between a charged surface and oppositely charged polyelectrolyte present in the aqueous phase. Protein is commonly used as the primary layer to obtain LBL emulsion (Gu et al., 2004; Gharsallaoui et al., 2010; Klein et al., 2010; Lim and Roos, 2015) as its charge can be modified by changing the pH of the aqueous phase. The isoelectric point (pI) of α-lactalbumin is 4.1 (Weinbreck et al., 2003) while β-lactoglobulin has pI of 5.2 (Bryant and McClements, 1998). On the other hand, gum Arabic has a pKa value of approximately 2.2 and will be negatively charged at above pH 2.2 (Weinbreck et al., 2004).

Spray drying is a dehydration method commonly utilized in the food industry as it is economical and straightforward producing high quality dry powders with long shelf-life. Besides freeze drying (Desorby et al., 1997; Harnkarnsujarit et al., 2012), spray drying is also used in the food industry for microencapsulation (Ré, 1998). Microencapsulation is a method where wall materials are used to entrap a core material to protect it from environmental stresses and to extend shelf life as well as provide controlled release of the core material (Shahidi and Han, 1993). Wall materials that have been used for spray drying include maltodextrins, trehalose, milk proteins, corn syrup and modified starch (Desorby et al., 1997; Hogan et al., 2001; Drusch et al., 2006; Shaw et al., 2007; Liang et al., 2013). However, crystallization of the glass formers; materials that are capable to form glassy structures in dried emulsions causes the release of the carotenoids containing lipid phase that will result in degradation of the carotenoids as a consequence of oxidation (Buera et al., 2005). Nonetheless, studies have shown that mixtures of amorphous sugars with high molecular weight carbohydrates can delay crystallization of the amorphous sugar (Mazzobre et al., 1997; Gabarra and Hartel, 1998; Kouassi and Roos, 2001; Potes et al., 2012). Our previous study showed that freeze-dried LBL emulsion with trehalose as the wall material gave a better protection towards the loss of carotenoids as compared to SL system (Lim et al., 2014). The objectives of the present study were to spray dry SL and LBL emulsions with high hydrophilic solids content, and to compare the ability of spray dried SL and LBL emulsions with mixture of maltodextrin and trehalose as wall materials in preventing the loss of carotenoids upon storage in the vicinity of the glass transition temperature of the encapsulant. The ability of humidified spray dried (HSD), non-humidified freeze-dried (NHFD), and humidified freeze-dried (HFD) systems in preventing the loss of carotenoids was determined as well. Data on carotenoid loss kinetics and the ability of SL and LBL systems to prevent losses of encapsulated carotenoids in spray dried systems during storage in closed containers were reported. These data are useful for formulated materials in food and pharmaceutical industries controlling the stability of oil soluble bioactive compounds. The study will provide information on the effects of glass transition on stability of encapsulated bioactives and the ability of SL and LBL systems in protecting bioactives. The use of high total solids emulsions for spray drying too will be beneficial for the industry as there are few reports on the use of such concentrated systems available.

2. Materials and methods

2.1. Materials

Whey protein isolate (WPI, Isolac) was obtained from Carbery Food Ingredients (Ballineen, Ireland), trehalose (crystalline dihydrate) from Hayashibara Shoji Inc. (Japan), maltodextrin (M100, DE 9–12) from Grain Processing Corporation (IA, U.S.A.), gum Arabic (Sigma Aldrich G9752) from Sigma Aldrich (Stenheim, Germany), sunflower oil from Musgrave Excellence™ (Spain), lutein (Marigold) from Shaanxi Sciphar Biotechnology Co. Ltd. (China) and all-trans-β-carotene (crystalline Type I, synthetic, > 93% (UV)) from Sigma–Aldrich (U.S.A.) All other chemicals were purchased from Sigma–Aldrich, Inc. (Dublin, Ireland).

2.2. Emulsion preparation

Deionized water was used to disperse WPI (10.71%, w/w, in water) and the dispersion was allowed to hydrate for 2 h to enhance hydration of the proteins. Citric acid solution (10% w/w) was used to adjust pH of the dispersion to pH 3.5. Sunflower oil containing β-carotene (0.05%, w/w, of oil) and lutein (0.05%, w/w, of oil) was prepared and mixed with a Silverson mixer (Model AXR, Silverson Machines Ltd., Chesham, UK) at 50 °C until a homogeneous dispersion was obtained. Pre-emulsion was obtained by mixing the oil phase and water phase using Silverson mixer at minimum speed for 60 s. The pre-emulsions were subsequently homogenized for 3 cycles at 240 bar (200 bars for the first stage and 40 bars for the second) at room temperature using a two-stage valve homogenizer (APV-1000, APV Homogenizer Group, Wilmington, MA, USA). Trehalose and maltodextrin (1:1, 57.14%, w/w, in water) were dissolved in water at 65 °C using a Silverson mixer. Maltodextrin was dissolved initially followed by trehalose and the pH was adjusted to pH 3.5 by citric acid solution (10% w/w). SL emulsion was obtained by mixing the emulsion to trehalose and maltodextrin solution for 30 min. Gum Arabic (2.91%, w/w, in water) was dispersed in deionized water and stirred for 2 h. Citric acid solution (10% w/w) was used to adjust pH of the dispersion to pH 3.5. To obtain LBL emulsion, the gum Arabic solution was mixed with the emulsion at room temperature for 30 min. The emulsion with gum Arabic as secondary layer was then mixed with trehalose and maltodextrin solution for 30 min.

2.3. Spray drying

The emulsions were dehydrated using a single stage Niro 25 spray dryer (GEA Niro, Soborg, Denmark) with rotating disc atomizer at 18,000 rpm. The inlet and outlet temperatures were 185 °C and 85 °C, respectively. The powders were rapidly cooled to room temperature, sealed in plastic bags, and stored at room temperature to prevent water uptake and physico-chemical changes prior to analysis. The powders (2 g) were then transferred into 10 mL clear glass vials (Schott, Müllheim, Germany) for further study.

2.4. Freeze-drying

Freeze-dried SL and LBL emulsions were prepared using a freeze-drier (Lyovac GT 2, Steris®, Hürth, Germany) by transferring 2.5 ml of aliquots of emulsions into 10 mL clear glass vials (Schott, Müllheim, Germany). The emulsions were diluted with 2.5 ml of water adjusted to pH 3.5 using citric acid solution to allow proper drying in the freeze-drier. The emulsions were frozen in vials at −20 °C overnight (HLLF-240, Heto, Jouan Nordic A/S, Allerød, Denmark) and then tempered at −80 °C in a deep freezer (Icebird/Mini Freeze 80, Heto, Jouan Nordic A/S, Allerød, Denmark) for 3 h before freeze-drying. Freeze-drying was done for at least 72 h under vacuum at pressure, $p < 0.1$ mbar. Samples obtained from freeze drying were used for HPLC analysis for up to 8 days (7 time points).

2.5. Samples packaging

A batch of spray dried and freeze-dried emulsions (SL and LBL) were humidified in vials over saturated solution of $MgCl_2$ (Sigma Chemical Co., St. Louise, MO, U.S.A.) at 0.33a_w in vacuum desiccators