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Thermoresponsive, water-dispersible microcapsules with a lipid-polysaccharide shell to protect heat-sensitive colorants

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ABSTRACT

We present a novel thermoresponsive microcapsule designed to protect heat-sensitive colorants from thermal degradation, with an aqueous core and a two-layer shell structure to ensure water-dispersibility. Surrounding the aqueous colorant core is a two-layer shell: an inner, solid lipid layer consisting of glycerol mono-oleate (GMO) and soy lecithin, and an outer, water-dispersible matrix consisting of maltodextrin and poloxamer 338. This thermoresponsive shell design is shown to prevent colorant fading due to heat degradation in a simulated pasteurization process. The encapsulated colorant produces a more intense beverage color compared to the non-encapsulated colorant. Simultaneously, the layered shell is shown to promote a homogeneous dispersion of the encapsulated color throughout an aqueous solution with no observed "creaming" or phase separation. As pasteurization is widely used in the food and beverage systems, this novel, multi-layer microcapsule design expands the applicability of heat-sensitive natural colorants in the food and beverage industry.

1. Introduction

Natural colorants are widely used in foods and beverages due to increasing consumer concerns about the safety of synthetic colorants (Katz & Williams, 2011). Natural colorants are extracted from fruit and vegetable sources, such as saffron, berries, annatto, and beetroot. Anthocyanin is a water-soluble flavonoid derived from red and blue parts of plants such as red cabbage leaves (Raheleh Ravanfar, Tamaddon, Niakousari, & Moein, 2016), berries (Zheng et al., 2013), and black carrots (Kammerer, Carle, & Schieber, 2004). It is one of the most commonly used colorants because of its vibrant color (Raheleh Ravanfar, Tamadon, & Niakousari, 2015). Norbixin is another water-soluble natural colorant extracted from the pericarp of the seeds of *Bixa orellana* L. shrub (Parvin, Aziz, Yusof, Sarker, & Sill, 2011). Both pigments have a wide application in soft drinks, ice cream, yogurt and yogurt drinks (Wallace & Giusti, 2008). Thermal degradation and photodegradation result in a color change for both anthocyanin and norbixin. This color change is due to the formation of different degradation products (Kechinski, Guimarães, Noreña, Tessaro, & Marczak, 2010). The application of these natural colors is therefore limited in foods and beverages that require thermal processing such as pasteurization or blanching (Khan et al., 2015). To increase the stability of natural colorants and broaden their potential application in the food industry, different methods, such as encapsulation and association reactions, have been developed (Celli, Ravanfar, Kaliappan, Kapoor, & Abbaspourrad, 2018; Chung, Rojanasasithara, Mutilangi, & McClements, 2017; Comunian, Ravanfar, Alcaine, & Abbaspourrad, 2018; Mehrad, Ravanfar, Licker, Regenstein, & Abbaspourrad, 2017; Ravanfar et al., 2016). Among these methods, encapsulation has recently received attention because it provides a physical barrier to protect the natural colors from degradation (Comunian et al., 2017a, 2017b; Raheleh; Ravanfar, Comunian, Dando, & Abbaspourrad, 2018a, 2018b; Sarkar et al., 2015; Torres et al., 1995). Different biopolymers have been used in encapsulation of natural colors (Raheleh Ravanfar, Celli, & Abbaspourrad, 2018a; Sakai, Sato, Masuda, Takeoka, & Tsuchida, 2008; Wu, Guan, & Zhong, 2015), with some studies reporting improved heat stability. One of the developed platforms for encapsulation of heat-sensitive compounds is a solid lipid particle, which improves heat- and photostability (Kumar, Abhijit, Medha, & Vandana, 2007). Employing this platform in a clear beverage product requires homogeneous distribution of particles in the beverage. However, solid lipid particles are prone to "creaming" or separation in beverage

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products, due to their lower density. As there is a great need to encapsulate natural colorants and protect against thermal degradation in beverage products, there is a corresponding need to improve the dispersibility of microcapsules in aqueous systems.

In this study, we present a novel thermoresponsive water-dispersible microcapsule to protect heat-sensitive compounds against thermal degradation. We design a core-shell structure with a shell containing a solid lipid layer and a water-dispersible polysaccharide layer, and an aqueous core containing heat-sensitive natural colors such as anthocyanin and norbixin. We use a water/oil/water (w/o/w) microemulsion dilution method to prepare the microcapsules. An aqueous solution of natural colors is dispersed in a combination of glycerol mono-oleate (GMO) and soy lecithin. Dispersing this w/o single emulsion in a secondary aqueous phase containing maltodextrin and poloxamer 338 at ambient temperature forms a solid lipid shell surrounding the aqueous core. Following a spray-drying step, a water-dispersible layer of maltodextrin and poloxamer is formed on the lipid shell. In this work, we show that GMO in a cubic crystalline phase in the lipid layer of microcapsule shell is able to protect the anthocyanin and norbixin from thermal degradation during the pasteurization process. We demonstrate that the maltodextrin layer of microcapsule shell increases the water-dispersibility of microcapsules in the beverage system. Using this strategy, the natural colorant is protected from fading, and the beverage color becomes more intense upon pasteurization process.

2. Materials and methods

2.1. Materials

Glycerol mono-oleate (Capmul GMO-50 EP/NF) with melting point of ~40 °C was kindly donated by Abitec Corporation (Columbus, OH, US). Soy lecithin (Yelkin™) was donated by ADM (Decatur, IL, US). Anthocyanin powder from the black carrot (ColorFruit® Red 122 WSP, Purity: 11.5%) and norbixin powder from annatto seeds (product number: 677837, purity: 15%) were kindly provided by Chris Hansen Laboratory A/S, Denmark. Maltodextrin (dextrose equivalent 13.0-17.0) and Poloxamer 338 (Pluronic® F108) were purchased from Sigma-Aldrich (St. Louis, MO, US).

2.2. Preparation of thermoresponsive microcapsules loaded with natural colors

Microcapsules were prepared using the microemulsion dilution method. Different formulations were examined to prepare microcapsules (data not shown), and the best formulation was selected. The best formulation was prepared in the following manner: Briefly, the lipid phase containing GMO: soy lecithin (2:1) was heated to 45 °C. The w/o single emulsion was prepared by dispersing the aqueous solution of anthocyanin (1 g/ml) or norbixin (0.04 g/ml) into the lipid phase (1: 3, aqueous phase: lipid phase) under stirring with magnet stirrer (CORNING, PC351, Corning, NY) at 1000 rpm. This w/o single microemulsion was dispersed in a secondary aqueous solution of pluronic F108 (1%) and maltodextrin (10%) (2: 5, w/o single emulsion: secondary aqueous solution) using a high-shear homogenizer (VWR 200 Homogenizer Unit, Randor, PA, USA) at 15000 rpm for 5 min to prepare w/o/w microemulsion. This w/o/w microemulsion was finally spray-dried at an outlet temperature of 50 °C, inlet temperature of 160 °C and flow rate of 3 L/h (Labplant Spray Dryer SD-Basic, Labplant, UK, Ltd. North Yorkshire, UK).

2.3. Characterization of microcapsules

2.3.1. Cryo-scanning electron microscopy (Cryo-SEM)

Using cryo-SEM images, the structure of the microcapsules was assessed. Cryo-SEM experiments were performed using a Quorum P3010 system (Qurorum Technologies, Newhaven, UK). The samples were plunge-frozen in liquid nitrogen, transferred under vacuum to the P3010, and coated with gold-palladium. Samples were maintained at -165 °C in the preparation chamber. The samples were transferred to the focused ion beam (FIB) to take images at -165 °C.

2.3.2. Size and zeta potential

The size and zeta potential of the microcapsules suspended in the deionized water (pH = 5.2) were measured with NanoZS90 zeta-sizer (Malvern 142 Instrument Ltd. UK) with a He/Ne laser ($\lambda = 633$ nm) at a fixed scattering angle of 90° at 25 ± 0.1 °C. The zeta potential values were automatically calculated from the electrophoretic mobility based on the Smouluchowski model (Fukui & Fujimoto, 2009). All measurements were performed in triplicate and reported as averages thereof.

2.3.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the microcapsules were investigated in the region from 4000 to 400 cm^{-1} (120 scans, resolution of 2 cm^{-1}) by IRAffinity- 1S Fourier Transform Infrared Spectrophotometer (Shimadzu Scientific Instruments/Marlborough, Massachusetts-USA).

2.3.4. X-ray diffraction (XRD)

X-ray diffraction measurements were performed using a Bruker D8 Advance ECO powder diffractometer (MA, USA). The generator was operated at 40 kV and 30 mA (Cu Ka radiation). Samples (spray-dried power of microcapsules) were scanned at room temperature from $2\theta = 2°$ to $2\theta = 45°$ under continuous scan in 0.02 step with 2θ min^{-1}.

2.3.5. Contact angle measurement of aqueous color solutions

The contact angle between the aqueous solution of colors (anthocyanin and norbixin) and the surface of the glass slide was measured using Ramé-Hart (Succasunna, NJ) Model 190 CA Goniometer. Droplets of the color solutions (4 μL each) were placed on the surface of the glass at room temperature, and the droplets' features were determined via image analysis. The subsequent contact angle values (θ) were calculated using the Ramé-Hart DROPimage CA software. Ten image-based measurements were taken, spaced by 1 s intervals. All reported θ values are averages of measurements in triplicate drop formation for each color solution.

2.3.6. Moisture content and water activity (a_w)

The moisture content of the samples was determined by drying the samples (1 g) at 105 ± 1 °C using a Denver Instrument IR30 Moisture Analyzer (Arvada, Co.) until a constant weight was attained. An AquaLab water activity meter (Model Series 3TE; Decagon Devices, Inc. Pullman, WA) was used to measure a_w of the samples at 25 °C.

2.3.7. Color content and encapsulation efficiency

Spray-dried microcapsules (0.05 g) were suspended in 1 ml deionized water and centrifuged (10 min, 0 °C, 17000 g). The non-encapsulated color was measured in the supernatant. To measure the entrapped color in the microcapsules, the pellet was dispersed in 1 ml ethanol, vortexed, centrifuged (10 min, 0 °C, 17000 g) and the encapsulated color was measured. The absorbance of the color solutions was measured using UV-Vis spectrophotometry (UV-Vis Spectrophotometer UV-2600, Shimadzu Scientific Instruments/