Food Hydrocolloids xxx (2014) 1–7

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Enzymatic digestible starch from pyrodextrinization to control the release of tocopheryl acetate microencapsulation in simulated gut model

Natthanan Subpuch [a], Tzou-Chi Huang [b], Prisana Suwannaporn [a, *]

[a] Department of Food Science and Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand
[b] Department of Biological Science and Technology, National Pingtung University of Science and Technology, Neipu 912, Taiwan

ARTICLE INFO

Article history:
Received 21 July 2014
Accepted 16 October 2014
Available online xxx

Keywords:
Pyrodextrinization
Microencapsulation
Release
Digestible starch
Rice starch

ABSTRACT

High amylose rice starch was modified using a pyrodextrinization process under conditions designed to avoid gelatinization of starch. Rice starch was hydrolyzed with 0.5% HCl and 0.5% citric acid solution at 130 °C for 1 h (H1), 2 h (H2), and 3 h (H3) respectively. Hydrolyzed starches (25% moisture content) were then Heat moisture treatment (HMT) at 115 °C for 1 h. Pasting properties, swelling power, solubility, crystallinity and *in vitro* and *in vivo* starch digestibility were investigated. Pyrodextrinized-HMT rice starch was then used as wall material for tocopheryl acetate encapsulation by spray drying. The encapsulation capacity, microstructure, *in vitro* releasing property under simulated gastric (SGF) and intestinal fluid (SIF) were measured. Results show an insignificant increased in rapid digestible starch (RDS) after pyrodextrinization. SDS drastically decreased in proportion to the increase in RS content. Blood glucose responses in Wistar rats fed with pyrodextrinized-HMT starch were slower than those fed with native starch. The pyrodextrinized-HMT starch microcapsule showed higher encapsulation capacity, better resistance to *in vitro* digestibility, prolonged release in SGF but higher release in SIF without changing its crystalline patterns.

1. Introduction

Criteria for an encapsulation wall material by spray drying are emulsion property, retention of core material and shelf life. Carbohydrates, such as starch, gum arabic and cyclodextrins, are commonly used. Hydrolyzed starches produced by hydrolyzing starch with an acid and/or an enzyme are less viscous at high concentration and have excellent protection (Jafari, Assadpoor, He, & Bhandari, 2008). High dextrose starch equivalent is less permeable to oxygen and shows high encapsulation efficiency. But hydrolyzed starch has poor retention behavior as it lacks emulsifying properties. A combination of wall materials, such as a blending of gum, maltodextrin and modified starch is used to improve this problem (Jafari et al., 2008). Acid modified tapioca starch is also reported to provide good retention of β-carotene (Loksuwan, 2007). Succinylated and phosphorylated rice starches are reported to use as wall materials for orange oil D-limonene (Verdalet-Guzmán, Martínez-Ortiz, & Martínez-Bustos, 2013). These starch derivatives exhibit good viscosity and high water absorption, resulting in high encapsulation efficiency. Octenylsucciniate starch (HI-CAP™100) was used for vitamin A and D-limonene encapsulation and showed high stability during spray drying and storage (Soottitantawat et al., 2005; Xie, Zhou, Liang, He, & Han, 2010).

Pyrodextrinization is involved in hydrolysis, transglucosidation and repolymerization of polymers. This chemical reaction is commonly used in the production of sweeteners, additives, binders and encapsulating agents. Pyrodextrinized starch exhibited high solubility, low viscosity and swelling power (Campechano-Carrera, Corona-Cruz, Chel-Guerrero, & Betancur, 2007). Lentil, sorghum, cocoyam, sagu, cassava and corn pyrodextrinized starches decreased enzymatically available starch and promoted non-digestible fractions (Kapuśniak & Jane, 2007; Laurentin, Cárdenas, Ruales, Pérez, & Tovar, 2003). Pyrodextinization of African locust bean can reduce swelling power, and increase solubility, resistant starch content and thermal stability (Sankhon et al., 2013). Cold-water soluble pyrodextrin from waxy maize starch also shows high solubility, as determined by small molecular fractions from acid attack in the amorphous and crystalline regions (Bai, Cai,

* Corresponding author.
E-mail address: prisana.s@ku.ac.th (P. Suwannaporn).

http://dx.doi.org/10.1016/j.foodhyd.2014.10.012
0268-005X/

Doutch, Gilbert, & Shi, 2014). Resistant starch (RS) can be prepared under heat and acid hydrolysis (Jochym, Kapusniak, Barczynska, & Śliżewska, 2012). High amylose rice starch was used as it can produce high RS (Zavareze & Dias, 2011). HMT was performed at a higher than gelatinization temperature but with limited water so starch does not gelatinize. This resulted in a more intact starch granule that still exhibited typical properties of starch.

In this study, pyrodextrinization together with HMT were applied to high amylose rice starch. This modified starch was intended to use as a wall material for encapsulation tocopheryl acetate by spray drying. The more orderly shorter chain starches are more digestible-resisted and could pass through a simulated gut system, hence prolong the release of a core material. Manipulation of the RDS, SDS and RS ratio in the pyrodextrinized-HMT starch was proposed to control the release of a core material in accordance with the digestion time and condition.

2. Materials and methods

2.1. Preparation of rice starch

High-amylose rice flour (Chainat 1 variety) was obtained as paddy rice from Chainat province rice seed center (Rice department, Ministry of Agriculture, Thailand). Paddies were dehusked and milled at 90 degree of milling. Polished rice grains were steeped in water for 4 h and then wet-milled using a double-disk stone mill (locally made in Thailand). Rice slurry was centrifuged using a basket centrifuge. The rice cake was then dried in a tray dryer at 40 ± 5 °C overnight until moisture content reached 10–14% (Cham & Suwannaporn, 2010). Rice starch was obtained by soaking rice flour in 0.05 M NaOH at a ratio of 1:2.5 (w:v), stirred at 3000 rpm for 3 h and then centrifuged at 3000 *g* for 20 min. The yellowish top layer was taken out and the process was repeated until the top layer was colorless. The precipitate was adjusted to pH 7 with 0.1 N HCl, washed several times with deionized water until neutral pH and then dried at 40 °C overnight to obtain 10–12% moisture content. Rice starch was milled and sieved using a rotor mill to obtain particle size of 100 mesh (SR 300, Retsch, Haan, Germany). Starch was kept in sealed polyethylene bag and stored at 4 °C until uses.

2.2. Pyrodextrinization process

Pyrodextrinized rice starch was prepared by spraying rice starch with 0.5% HCl solution (w/w) to a final concentration of 1% (w/w) of starch (dry basis) followed by 0.5% citric acid solution (w/w) to a final concentration of 1% (w/w) of starch (dry basis) (modified from Jochym et al., 2012). Sample was then mixed and dried at 50 °C until moisture content was below 5% (w/w). The sample was put in a screw cap glass bottle and heated at 130 °C for either 1 h (H1), 2 h (H2) and 3 h (H3) and then cooled down in a desiccator. The obtained starch was then washed with 95% ethanol several times until pH 7, dried at 50 °C overnight and then dried at 110 °C for 1 h. Samples were milled to a particle size of 100 mesh. Sample was kept in a sealed polyethylene bag and stored at 4 °C until use.

Pyrodextrinized rice starch was determined by its glass transition temperature (Tg) using a differential scanning calorimeter (DSC) (Star® System; Mettler Toledo AG, Greifensee, Switzerland). DSC was previously calibrated using indium and zinc standards. The hydrolyzed starch sample (25% moisture content) was heated from 25 °C to 95 °C at 1 °C/min increasing rate. Sample was cooled down immediately to 5 °C at 20 °C/min rate. It was then reheated at rate 1 °C/min. Tg appeared as the peak point on the first derivative curve in a thermogram. The temperature at the midpoint of the change in slope was taken as Tg (Cham & Suwannaporn, 2010).

2.3. Heat moisture treatment (HMT) of the pyrodextrinized rice starch

Pyrodextrinized rice starch was hydro-thermal modified using a temperature above its glass transition (Section 2.2) and gelatinization temperatures but with limited moisture content so the starch did not gelatinize. Pyrodextrinized rice starch was adjusted to a moisture content of approximately 25% and equilibrated in a desiccator until stable moisture content was obtained. It was then put in a screw cap glass bottle to maintain its moisture and then heated at 115 °C for 1 h. The pyrodextrinized-HMT rice starch was cooled down in a desiccator and kept in a sealed polyethylene bag at 4 °C until next use.

2.4. Tocopheryl acetate encapsulation by spray drying

Pyrodextrinized-HMT rice starch was used as a carrier or encapsulation wall material for spray drying. Wall materials; gum arabic, pyrodextrinized-HMT rice starch and maltodextrin (DE 10), were dry mixed at a ratio of 4:1:1 (by weight) (modified from Kanakdande, Bhosale, & Singhal, 2007) (Table 1). The dry mixture was then suspended in distilled water at 30% (w/v) using an overhead stirrer and kept overnight in a refrigerator (4 °C) to complete swelling. Load of core material was calculated as percent dry weight of carrier. Tocopheryl acetate (Sigma Aldrich Co., Ltd. Thailand) (10% by weight of carrier) and Tween 80 (Siam Victory Chemicals, Thailand) (0.2% by weight of carrier) were mixed with the prepared suspension using a two stage high pressure homogenizer (15MR-8TA, APV Gaulin, Inc., Wilmington, MA, USA) at 5000 psi to obtain a stable emulsion (modified from Kanakdande et al., 2007). Slurry was immediately spray dried at 160 ± 5 °C inlet temperature and 90 ± 5 °C outlet temperature. Microcapsules were collected from the collecting chamber and kept in a sealed, airtight pouch. These pouches were stored in a desiccator until needed.

2.5. Determination of pyrodextrinized-HMT rice starch properties

2.5.1. Pasting properties

Pasting properties of all starch samples were measured using a Rapid Visco Analyser (Newport Scientific, Australia). Starch (3 g, 14% wb) was mixed with distilled water (25 mL) in a metal RVA canister. Heating pattern followed a rice starch profile (AACC Method 61-02, 2000).

2.5.2. Swelling power and solubility

Rice starch sample (0.5 g) was mixed with 15 mL distilled water. The suspension was heated at 55, 65, 75 and 85 °C for 30 min. The gelatinized sample was cooled down and centrifuged at 2200 g for 15 min. The supernatant was dried at 100 °C and weighed to quantify solubility. The sediment was weighed to quantify swelling power. Calculations are as followings.

(i) Swelling power = weight of sediment/weight of dried starch
(ii) % Solubility = (weight of dried solid in supernatant/weight of dried starch) × 100

2.5.3. In vitro starch digestibility

Porcine pancreatin (0.45 g) (EC 232.468.9, 30,000 BPU/g; Sigma Aldrich Co.,Ltd, Thailand) was dispersed in water (4 mL) and centrifuged at 1500 g for 10 min. The supernatant (2.7 mL) was

Please cite this article in press as: Subpuch, N., et al., Enzymatic digestible starch from pyrodextrinization to control the release of tocopheryl acetate microencapsulation in simulated gut model, *Food Hydrocolloids* (2014), http://dx.doi.org/10.1016/j.foodhyd.2014.10.012