Carbohydrate Polymers 198 (2018) 473–480

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Physicochemical properties and flavor retention ability of alkaline calcium hydroxide-mungbean starch films

Wathanamon Chanjarujit[a,b,*], Parichat Hongsprabhas[a,b], Siree Chaiseri[a,b]

[a] Department of Food Science and Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand
[b] Center of Advanced Studies for Agriculture and Food, Kasetsart University Institute for Advanced Studies, Kasetsart University, NRU-KU, Bangkok 10900, Thailand

ARTICLE INFO

Keywords:
Starch
Calcium
Physicochemical properties
Flavor retention

ABSTRACT

The physicochemical properties and the flavor retention ability of the dried mungbean starch film formed in the presence of calcium ions under alkaline pH were analyzed. Treating starch in a NaOH or $Ca(OH)_2$ solution at pH 12 induced the formation B-type starch crystal. However, the starch film made with $Ca(OH)_2$ (Ca-film) was more effective than starch film made with NaOH (Na-film) in entrapping 1,8-cineole, menthone and citonellol. Entrapment efficiency of citonellol in Ca-film which had B-type starch crystal structure was close to that of the V-type starch film formed at neutral pH using distilled water (DW-film). 1,8-cineole, menthone, and citronellol were entrapped in dried Ca-films for 5.07%, 1.52%, and 30.84%, respectively. Physical entrapment of flavor compounds by alkaline-treated starch and high water solubility (24.4–46.7 %) of Ca-films could help designing a novel controlled flavor release systems.

1. Introduction

Binding flavor compounds to starch in food processing occurs in several ways. Starch gelatinization leads to inclusion complexes with flavors through amylose helices, creating a hydrophobic interior where the number of glucose molecules per helix turn depends on the flavor molecule's characteristics (Taylor, 1999). This structure is generally known as V-amylose. After gelatinization, many starchy foods are further processed to reduce moisture content and create attractive textures, qualities preferred for biscuits, snacks, and cereals. Physical entrapment is a particularly important interaction between starch and flavor compounds in these low moisture starch products (Escher, Nuessli, & Conde-Petit, 2000).

Flavor retention behavior is affected by the type of starch-flavor interaction within the starch matrix. The classical V-amylose complex is capable of decreasing flavor compound volatility while increasing its thermal stability. Alternatively, the polar interaction between starch and flavor via hydrogen bonding is sensitive to water. The moisture absorption could accelerate the loss of entrapped flavor from the starch matrix due to broken hydrogen bonds (Arvisenet, Le Bail, Voilley, & Cayot, 2002; Obiro, Sinha Ray, & Emmambux, 2012). Understanding starch-flavor interaction is useful for improving food quality and developing new flavor encapsulation carriers (Jouquand, Ducruet, & Le Bail, 2006).

Lime or calcium hydroxide, $Ca(OH)_2$, is widely used in the preparation of starch-based foods in South America and Asia. It is used to promote sustained crispness in fried batter or pastry/dough, facilitate the maize pericarp removal for further processing in wet or dry milling for dough or masa production. The effects of $Ca(OH)_2$ on starch properties depend on its concentration. At low $Ca(OH)_2$ concentrations ($< 0.4\%$), granule crystalline regions were disrupted and the exchange of protons for Ca^{2+} ions stretched the granule matrix. The starch granules were more susceptible to enzyme attack, held more water, swelled to a greater extent, and produced greater viscosity as compared to starch cooked in water.

At high $Ca(OH)_2$ concentrations ($> 0.4\%$), Ca-starch crosslinks stabilized the granules, reversing the trend mentioned above (Bryant & Hamaker, 1997). A schematic representation of ionic crosslinks between calcium and starch in an alkaline system has been published by Wing, Maiti, and Doane, (1987). Starch hydroxyl groups have a greater propensity to ionize in high pH conditions (pH $>$ 12), creating binding sites for Ca^{2+} ion interaction. This produces both calcium crosslinking between ionized starch $-OH$ groups, as well as generating Ca^{2+}-induced starch aggregates (Israkarn & Hongsprabhas, 2017; Israkarn, Hongsprabhas, & Hongsprabhas, 2007). For several South-East Asian starch-based desserts, a saturated solution of $Ca(OH)_2$, with a pH of around 12.2, is a commonly used functional ingredient to give cohesiveness and firmness of such desserts (Pookidakan & Jangchud, 2014). It was noticed in our laboratory that these desserts had long-term flavor retentions. However, the nature of the interactions between flavor

* Corresponding author at: Department of Food Science and Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand.
E-mail addresses: wathanamon.c@ku.th (W. Chanjarujit), parichat.h@ku.ac.th (P. Hongsprabhas), siree.c@ku.ac.th (S. Chaiseri).

https://doi.org/10.1016/j.carbpol.2018.06.118
Received 30 March 2018; Received in revised form 27 June 2018; Accepted 27 June 2018
Available online 30 June 2018
0144-8617/

compounds, Ca^{2+}-induced starch aggregates and matrices in the presence of $Ca(OH)_2$ solution remain unknown, requiring further study.

Mungbean starch was chosen as the model starch matrix, being an economical, high amylose content starch (31–38%) compared to other commercial starches in Asia, such as corn (17–22% amylose), rice (21–25% amylose) or tapioca (18–24% amylose) starches (Jane, 2009). High amylose starch has beneficial film-forming properties, providing a close packing network for potentially reduce the loss of flavor molecule from the starch film compared to starch with low amylose content (Wing et al., 1987). Keatkrai, Lumdubwong, Chaiseri, and Jirapakkul, (2017) have also demonstrated that mungbean starch can be used to encapsulate menthone via V-type starch crystal structure provided that mungbean starch was gelatinized at 140 °C for 1 h. to form inclusion complex with menthone.

In this research, we hypothesized that Ca^{2+}-induced aggregation of starch could allow the starch chains to pack closely and assist physical entrapment of flavor molecules in the starch film. Such mechanism could entrap the flavor in different fashion compared to starch inclusion complex. This is because charge repulsion of ionize OH groups could prevent the formation helical structure to the extent that inclusion complex can be formed as required in V-starch crystal structure.

This research focused on the role of Ca^{2+} under alkaline condition on the retention of flavor compounds in starch film. The comparison among starch films prepared at neutral pH using distilled water, and alkali pH using NaOH or $Ca(OH)_2$ in flavor entrapment was investigated. The insights may help designing novel flavor encapsulation techniques using Ca^{2+}-induced starch aggregate.

2. Materials and methods

2.1. Materials

Mungbean starch (Sithinan, Bangkok, Thailand) was purchased locally and found to have an amylose content of 32.9%. NaOH was obtained from Merck (Darstarchtadt, Germany), and $Ca(OH)_2$ was supplied by Ajax Finechem (Auckland, New Zealand). Three types of flavor compound that are stable in an alkaline condition (from the preliminary test) and have relatively similar molecular weights, were selected as flavor models containing: 1,8-cineole (Aldrich, purity > 99%), menthone (Aldrich, purity > 90%) and citronellol (Aldrich, purity > 95%). Their physicochemical properties are shown in Table 1. All were purchased from Sigma-Aldrich (St.Louis, MO, USA).

2.2. Preparation of starch films

Starch films were prepared with three different solutions: $Ca(OH)_2$ solution (alkaline solution with Ca^{2+}), NaOH (alkaline solution without Ca^{2+}) and distilled water (neutral solution) and three types of flavor compound: 1,8-cineole, menthone or citronellol were used as flavor models. The $Ca(OH)_2$ concentration solution used was 1.3 g/L (w/v), with a pH value of 12, similar to that of lime solutions generally used in Southeast Asian households. The NaOH solution was prepared at the same pH level (4 g/L, pH 12). Distilled water (pH ~ 7) was used to prepare the reference dried starch film. In this research, the starch films were prepared by casting and drying into films using method described by Israkarn and Hongsprabhas (2017) to ease preparation and parameter measurements.

Two grams of starch was dispersed in three 100 mL solutions each (1.3 g/L $Ca(OH)_2$, 4 g/L NaOH or distilled water). The starch suspensions were gelatinized in a water bath at 95 °C for 30 min and then were cooled to 30 °C. For samples with the incorporation of flavor compounds, 260 mg of 1,8-cineole, menthone or citronellol was individually added to each solution. The film-forming solutions were poured into a Teflon-coated tray and dried using a tray dryer at 40 °C for 32 h to obtain the dried starch films made of $Ca(OH)_2$ solution (Ca-film), NaOH solution (Na-film), and distilled water (DW-film), with and without flavor compounds. The samples were prepared in triplicate and were cut into 5 mm × 5 mm squares for further analysis. The dried starch films contained 10–12% moisture content.

2.3. X-ray diffraction (XRD)

XRD patterns of starch films, with and without flavor compounds, were evaluated by a Bruker D8 Advance (Bruker Corporation, Germany). The samples were scanned over a diffraction angle range of 2θ = 5–60° at 2° per min with a 0.03° step size. The relative crystallinity percentage of starch was calculated as the ratio of the area above a smooth curve of connected peak baselines to the total area over the diffraction angle range of 2θ = 9–30°. The data were analyzed by Diffrac.Suite EVA software (Bruker Corporation, Germany).

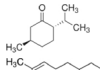
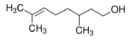
2.4. Determination of entrapped flavor compounds

Before determining the amount of entrapped flavor compound in starch films, the excess flavor compound on the film surface was removed by hexane washing (Keatkrai et al., 2017). The solvent-washed samples (0.25 g) were dispersed in 1 N NaOH solution and the entrapped flavor compounds were extracted by hexane and quantitated by gas chromatography (GC) (Tapanapunnitikul, Chaiseri, Peterson, & Thompson, 2008). 2-Methyl-3-heptanone (15 mg) was used as an internal standard. The GC (6890 N; Agilent Technologies, Santa Clara, CA, USA) was equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector. The oven temperature program was held at 40 °C for 2 min, heated to 180 °C at a rate of 5 °C/min, heated further to 250 °C in 2 min, and held at 250 °C for 3 min. The flavor entrapment (%) and the entrapment efficiency (%) were determined as follows:

$$\text{Flavor entrapment (\%)} = \frac{\text{weight of entrapped flavor in film}}{\text{weight of film}} \times 100$$

$$\text{Entrapment efficiency (\%)} = \frac{\text{weight of entrapped flavor}}{\text{weight of flavor added initially}} \times 100$$

Table 1
Physicochemical properties of flavor compounds.

Compound	Chemical structure	Molecular weight (g/mol)	Boiling point (°C)	Log P^a	Water solubility (g/L) at 25 °C	Vapor pressure (mmHg) at 25 °C
1,8-cineole		154.25	176	2.84	3.10	1.65
Menthone		154.24	208	3.05	0.49	0.26
Citronellol		156.27	222	3.91	0.20	0.02

[a] Log P = Log partition coefficient of a compound between octanol and water.