



Digestibility and physicochemical properties of starch-galactomannan complexes by heat-moisture treatment

Yun Chen¹, Xiaoya Xiong, Qunyu Gao*

Carbohydrate Laboratory, College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, PR China

ARTICLE INFO

Article history:

Received 11 July 2017

Received in revised form

17 November 2017

Accepted 18 November 2017

Available online 21 November 2017

Keywords:

Maize starch
Galactomannan
HMT
Digestibility

ABSTRACT

Native maize starch blended with galactomannan (NS-GM) was used to produce starch-galactomannan complex with heat-moisture treatment (HMT). In-vitro digestibility and physicochemical properties of starch and starch-galactomannan complexes were investigated. It was found in this research that the resistant starch content in the HMT NS-GM composite particles was related to the ratio of galactose/mannose residues in the galactomannan. The resistant starch content was presented in the order of HMT starch-locust bean gum complex, HMT starch-Tara gum complex, HMT starch-Guar gum complex, and the resistant starch content of HMT starch-Tara/Guar composite significantly increased with the amount of gum increased. Moreover, the resistant fragment in the resulting composites was more than that in the native and HMT starches. Scanning electron microscopy (SEM) showed that the degree of attachment of galactomannan to starch was also positively correlated with the galactose/mannose residue ratio of galactomannan and the phenomena became more obvious with the increase in the addition amount of the gums. X-ray diffraction results showed that the crystal forms of HMT starch and HMT NS-GM were the same as the maize starch. Differential scanning calorimetry (DSC) determination showed that the crystal structure of starch become stabler after heat-moisture treatment and the addition of galactomannan, but the double helix structure and the crystallization area was reduced. HMT NS-GM formed relatively looser recrystallization structure after refrigerated storage.

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1. Introduction

Starch is the second abundant natural polymer, which is the main carbohydrate in human nutrition and widely used in industry (Lehmann & Robin, 2007). However, there are many defects in the use of starch, such as easily regeneration and gelatinization, low solubility, poor heat and shear resistance and textural change (Kamm, Gruber, & Kamm, 2006; Lawal, 2009; Singh, Kaur, & Mccarthy, 2007; Wang et al., 2009). To overcome these shortcomings, starch is modified or compounded with non-starch hydrocolloids to improve its properties according to the application (Lee, Baek, Cha, Park, & Lim, 2002; Mali et al., 2003).

Non-starch hydrocolloids is widely used in the food to improve the stability and texture, and it is also often known as thickener or gelling agent (Chung, Liu, & Lim, 2007). Due to the high water solubility and being resistance to digestive enzymes, most gums

rarely digested in human upper intestines, thus providing the same physiological effects as dietary fibers (Chung et al., 2007; Dartois, Singh, Kaur, & Singh, 2010; Hang et al., 2015). Furthermore, the nutritional impact of the interaction between starch and non-starch hydrocolloids has become a vital issue in improving the nutritional benefits of starch and food in relation to their ability to alter the amount of starch hydrolysis (Brennan, 2005). In addition, many researchers studied the structures and physicochemical properties of the starch and gum complexes. Hussain et al. (Hussain, Vatankhah, Singh, & Ramaswamy, 2016) found that the gums increase starches stabilities toward various physical changes during processing (heat, shear, and acidic medium). von Borries-Medrano et al. (von Borries-Medrano, Jaime-Fonseca, & Aguilar-Méndez, 2016) treated the corn starch and guar gum complex with dry heating, and found that the crystal structure of corn starch changed. And treating the waxy corn starch and xanthan gum complex with dry heating, the size of waxy starch granules increased owing to the crosslinking effect between starch and xanthan gum (Li et al., 2013). Guar gum can increase the peak viscosity, final viscosity, collapse value and recovery value of rice

* Corresponding author. Tel.: 8613660261703; fax: 0086 2087113848.

E-mail addresses: sksp081cy@163.com (Y. Chen), qygao@scut.edu.cn (Q. Gao).

¹ Tel.: 8613570931270; fax: 0086 2087113848.

starch (Kim & BeMiller, 2012; Kim, Patel, & BeMiller, 2013). Muadklay (Muadklay & Charoenrein, 2008) found that the addition of four hydrocolloids was effective in stabilizing tapioca starch gels in different ways, xanthan gum was most effective in reducing syneresis, and locust bean gum is more effective in retarding retrogradation than konjac-glucomanna.

Galactomannan is a polysaccharide consisting of galactose and mannose residues. Guar, tara and locust bean gum are common galactomannan species, which are nonionic polysaccharides, and the ratio of galactose to mannose is 1:2, 1:3 and 1:4 respectively. Galactomannans are widely used in food as thickeners, stabilizers and water holding agents.

Heat-moisture treatment (HMT) is one of the most important physical methods used to modify starch without destroying its granular structure. It treated the starch granules (18%–27%), w/w and at a temperature (90–120 °C) above the glass transition temperature (T_g) but below the gelatinization temperature. Researches had found that the HMT would change the morphology, X-ray diffraction pattern, thermal properties, pasting properties and enzyme digestibility of starches (Hoover, 2010; Jiranuntakul, Puttanlek, Rungsardthong, Pancha-arnon, & Uttapap, 2011). The aim of this study was to prepare the heat-moisture treated starch-galactomannan complex (HMT NS-GM), and study the effects of different gums on the granule structure, crystal structure and in vitro digestibility of normal corn starch by comparing the effects of three different gums, that was guar gum, tara gum and locust bean gum. Moreover the mixtures were heat-moisture treated starch-guar (HMT NS-Guar), heat-moisture treated starch-tara (HMT NS-Tara) and heat-moisture treated starch-locust bean (HMT NS-LBG). The distribution of galactomannan and starch complex was studied by comparing in vitro digestion of the complex, the morphology, X-ray diffraction analysis, swelling power and solubility analysis, thermal properties, and refrigerated-storage-retrogradation analysis, the effects of different galactose, mannose residue ratio, and the amount of different gums added to the complex were also studied.

2. Materials and methods

2.1. Materials

Maize starch was purchased from Qinhuangdao Lihua Starch Co., Ltd, China. Locust bean gum (LBG) was obtained from Henan Annist Food Co., Ltd, China. Tara gum (Tara) and guar gum (Guar) were obtained from Zhaoqing Hongfa Biological Technology Co., Ltd. Glucose oxidase-peroxidase (GOPOD) assay kit was sought from Megazyme International Ireland Limited. Pancreatic alpha-amylase (16 units/mg) and amyloglucosidase were purchased from Sigma-Aldrich Chemical Company (St. Louis, USA). Chemicals and solvents used in this work were of analytical grade.

2.2. Preparation of starch-galactomannan complex by heat-moisture treatment

Galactomannan was dispersed in distilled water (190 mL) with vigorous stirring by 250 rpm at 90 °C water bath. After the gum was completely dissolved, and then cooled. Starch (50 g dry basis) was added to the prepared gum solutions and stirred for 40 min at room temperature and then transferred to a glass dish and dried at 45 °C in a convection oven until the moisture content reached about 20% through gravimetrically determination and grounded into powder. The blend powder was transferred to a polytetrafluoroethylene tube and sealed in a reaction kettle at 120 °C for 4 h and then dried at 45 °C. The dried starch gum mixture was ground to a powder and passed through a 100-mesh. The addition amount of

galactomannan was 0, 0.5%, 1% and 2% of the dry weight of starch, respectively.

2.3. In-vitro digestibility of starch samples

The digestibility of not gelatinized samples was determined by the Englyst method (Englyst, Kingman, & Cummings, 1992) with some modifications. The enzyme solution was prepared by suspending pancreatin (1.5225 g, 8 × USP) in sodium acetate buffer (7.5 mL, 0.1 M, pH 5.0) with magnetic stirring for 30 min, and then centrifuged for 10 min at 1500 g. The supernatant was transferred into a beaker and mixed with 0.75 mL of amyloglucosidase (300 U/mL) before use (Shi, Chen, Yu, & Gao, 2013). Starch (200 mg dry basis) was added in 50 mL centrifuge tube with 15 mL sodium acetate buffer solution (0.2 M, pH5.2), and stirred for 40 min at room temperature at 37 °C. Followed by an equilibration at 37 °C for 10min, and then 5 mL mixture of pancreatic alpha-amylase and amyloglucosidase was added. Enzyme digestion was carried out in a 37 °C water bath at 150 rpm, and 0.5 mL aliquots of hydrolyzed solution were collected at 20 and 120 min. Then 20 mL of ethanol (95%) was added to the aliquots to deactivate the enzyme. After centrifugation (1500 g, 10 min), the glucose content was determined using the glucose oxidase/peroxidase (GOPOD) assay kit. The percentage of hydrolyzed starch was calculated by multiplying the glucose content by a factor of 0.9, which was the molar mass conversion from glucose to anhydroglucose (the starch monomer unit). The values of RDS, SDS and RS were obtained by combining the values of G_{20} (glucose released at 20 min), G_{120} (glucose released at 120 min), FG (free glucose) and TS (total starch) using the following formulae:

$$RDS = 0.9 (G_{20} - FG) / TS \times 100\%$$

$$SDS = 0.9 (G_{120} - G_{20}) / TS \times 100\%$$

$$RS = 1 - (RDS + SDS) = 1 - 0.9 (G_{120} - FG) / TS$$

2.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to analyze the micro-morphology of native and modified maize starch. Starch samples were scattered on double-sided adhesive tape attached to a circular aluminum stub, and coated with 20 NS gold under vacuum. After then, the samples were viewed and photographed with a scanning electron microscope (model EVO 18, Zeiss, Germany) at an acceleration potential of 20 kV.

2.5. X-ray diffraction (XRD) pattern

The sample should be first placed in a relative humidity of 15% of the dryer for 24 h to balance the water, so that all samples of the same moisture content. X-ray diffraction (XRD) pattern of different samples were obtained with a D/Max-2200 X-ray diffraction (Rigaku Denki Co., Tokyo, Japan) using Cu Ka radiation at 44 kV and 26 mA. The diffraction angle ranged from 4° to 40° (2 θ) at the rate of 5°/min (Yanika, Chureerat, Vilai, & Dudsadee, 2009). Relative crystallinity was calculated based on the method described by the ratio of the crystalline area to the total diffractogram area (Nara, Sakakura, & Komiya, 1983).

2.6. Swelling power and solubility index determination

The swelling power and solubility of starch and NS-GM complex

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