Food Hydrocolloids 55 (2016) 172–178

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Preparation and properties of RS4 citrate sweet potato starch by heat-moisture treatment

Huiping Xia, Yunyun Li, 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 7 April 2015
Received in revised form
29 October 2015
Accepted 4 November 2015
Available online 7 November 2015

Keywords:
Citric acid
Heat-moisture treatment
Resistant starch

ABSTRACT

Sweet potato starch (SPS) granules were firstly subjected to heat-moisture treatment (HMT) and then esterified with citric acid (CA). The physicochemical properties of CA-starch and heat moisture treatment citric acid starch (HMT-CA-starch) were investigated. Results showed that the high dosage of CA significantly increased the degree of substitution (DS) and the resistant starch (RS) content of the CA-starch ($P < 0.05$). With HMT, the RS content of HMT-CA-starch was effectively increased compared to the controls. Scanning Electron Microscopy (SEM) pictures showed that the shape and integrity of HMT-starch granules did not change but concavity was observed. However, CA-starch and HMT-CA-starch appeared collapses and fragments. The spectra of Fourier-transform infrared spectroscopy (FT-IR) indicted that the esterification of HMT-CA-starch was stronger than the CA-starch. Crystal structure of CA-starch remained unchanged, while that of HMT-CA-starch changed from A-type to C-type compared to HMT-starch. The relative crystallinity (RC) of HMT-starch, CA-starch and HMT-CA starch was decreased. The gelatinization temperatures (T_o, T_p, and T_c), enthalpy of gelatinization (ΔH) and swelling power decreased sharply in all CA-starches compared with the controls. All results indicated that HMT increased the accessibility of the starch granules and made it easier for CA to penetrate into the starch granules.

1. Introduction

There is a growing consumer demand and increasing attention for high quality functional food (Lopez-Rubio, Gavara, & Lagaron, 2006). The food industry is targeted to produce some inventive substances that can be added to food with health benefits. Carbohydrate such as starch is one of the major sources of energy, which can be widely used in food and nonfood application. However, native starches usually could not meet the demands of the industries. Therefore, starches have been modified chemically and physically in order to extend the starch applications range in other areas (Chung, Hoover, & Liu, 2009). During the recent decades, one of the new rising stars which favored many research workers and enterprises is resistant starch (RS).

RS has been defined as the starch fraction which escapes digestion in the small intestine of healthy individuals (Englyst, Kingman, & Cummings, 1992). It is well-known and documented that RS plays a very important role in functional food which includes reducing the glycemic response, acting as a functional prebiotic for some probiotic microorganisms and increasing the production of short chain fatty acids in the large intestine. RS is also important in the diet because of its interactions with other dietary components, including not only macronutrients such as fats and protein but also micronutrients such as minerals (Asp, Van Amelsvoort, & Hautvast, 1996; Kendall, Emam, Augustin, & Jenkins, 2004; Nugent, 2005). RS appears to possess a unique combination of physiological and functional properties compared to traditional types of fibers, which are generally associated with a coarser texture (Baixauli, Salvador, & Fiszman, 2007).

According to the report of Englyst et al. (1992) and Tovar (1992), RS can be classified into four types, physically inaccessible starch (RS1); RS granules (RS2); retrograded starch (RS3); chemically modified fragments (RS4). The chemically modified starch gained great attentions among them, because it can be prepared by a variety of different chemical reactions such as esterification (Wootton & Chaudhry, 1979; Xie, Liu, & Cui, 2006), etherification (Leegwater & Luten, 1971), and cross-linking (Janzen, 1969; Luo, Huang, Fu, Zhang, & Yu, 2009). Due to these chemical substitutions of starch could sterically hinder the attack of enzymes, the modified starch

* Corresponding author.
E-mail addresses: shaouping88@163.com (H. Xia), qygao@scut.edu.cn (Q. Gao).

http://dx.doi.org/10.1016/j.foodhyd.2015.11.008
0268-005X/

could not be degraded completely (Björck, Gunnarsson, & Østergård, 1989). Compared to many other substances used for chemical modification of starch, citric acid (CA) is of low toxicity and can enhance the metabolism in our body (Anastassiadis, Morgunov, Kamzolova, & Finogenova, 2008; Klaushofer, Berghofer, & Steyrer, 1978).

Heat-moisture treatment (HMT) refers to a physical modification technique that involves treatment of starch granules at low moisture levels (<35% moisture, w/w) for a certain time period (15 min–16 h) and at temperatures (84–120 °C) above the glass transition temperature (T_g) but below the gelatinization temperature (Jacobs & Delcour, 1998). There were a lot of literature reported that HMT could change various properties of the starch such as swelling factor, gelatinization temperatures, X-ray diffraction pattern and crystallinity and gelatinization parameters (Donovan, Lorenz, & Kulp, 1983; Gunaratne & Hoover, 2002; Kawabata et al., 1994; Kulp & Lorenz, 1981). The starch modified by HMT is more receptive to the consumers due to its special physicochemical properties, moreover physical modifications usually are considered to be more natural and safe.

Although the synthesis and physicochemical characteristics of CA-starch have been studied extensively (Hung, Vien, & Phi, 2016; Reddy & Yang, 2010; Shin et al., 2007; Xie & Liu, 2004; Yu, Wang, & Ma, 2005), little work has been reported on the structure and properties of starch modified with CA after hydrothermal pretreatment. We suppose that the swelled starch after HMT may increase the reactivity of the starch granules and make the CA easier to access to the starch granules. The objective of this study was to prepare a kind of RS using CA with HMT, and the physicochemical properties of the products were investigated.

2. Materials and methods

2.1. Materials

Sweet potato starch was supplied by Quxian national grain storage (Sichuan, China). RS assay kit, including pancreatic α-amylase, amyloglucosidase and Glucose-oxidase-peroxidase-aminoantipyrine (GOPOD) reagent enzymes, was purchased from Megazyme International Ireland Limited (Wicklow, Ireland). CA and all other chemical compounds were of analytical grade reagents.

2.2. Preparation of CA-starch

CA-starch was produced based on the method of Klaushofer, Berghofer, and Pieber (1979) with some modifications. The sweet potato starch (50 g, dry basis) was added to a different volume of the CA solution (50%, w/w). The dosage of the CA was as to 10%, 20%, 30%, 40%, 50% and 60% of starch dry weight, respectively. After stirred evenly, the suspension was adjusted to pH 3 with 10 M NaOH, then was transferred to a stainless steel tray and left for 16 h at 25 ± 2 °C. The tray was then placed in an air oven (DHG-9140A Shanghai Shengxian Instrument Manufacturing Company, China) and dried at 45 °C for 12 h to a moisture level of 5%–10% (w/w). Each reaction condition was performed in triplicate. The mixture was ground and dried in an air oven for 4 h at a temperature of 140 °C. The dry mixture was washed with 3 L water to remove the unreacted CA and then washed once with absolute ethanol. The washed starch was air-dried at 45 °C for 24 h and finally ground into powder using a grinder.

2.3. Preparation of HMT-CA-starch

The moisture levels of native starch samples were adjusted to 20%, 25%, 30% and 35%. All samples were then held in sealed containers (400 mL) and kept for 12 h at the 25 ± 2 °C. The sealed containers were heated in an air oven at 120 °C for 12 h. All samples were removed from the containers after cooled to 25 ± 2 °C and dried at 45 °C for 12 h to achieve a uniform moisture content (~8%). Based on the moisture content before treatment, the HMT-starch samples will be referred to as HMT-20, HMT-25, HMT-30 and HMT-35.

The heat-moisture treated sweet potato starch (50 g, dry basis) was added to 50% CA solution (50 mL). After stirring evenly, the mixture was adjusted to pH 3 with 10 M NaOH. The next process mode were as the same as in Section 2.2.

Starches without HMT were used as controls following the same procedure.

2.4. Determination of RS content

RS content was analyzed using RS assay kit based on the Method of 2002.02 of the Association of Official Analytical Chemists AOAC (McCleary, McNally, & Rossiter, 2002). Starch sample (100 mg, dry basis) was equilibrated horizontally in a shaking water bath with 4.0 mL enzyme mixture (pancreatic α-amylase, 10 mg/mL; amyloglucosidase, 3 U/mL) for 16 h (37 °C, 200 r/min). Afterwards, 4.0 mL ethanol (99%, v/v) was added to terminate reaction and the obtained residue was washed twice with ethanol (50%, v/v), then treated with KOH solution (4 M, 2 mL) in ice bath for 20 min to solubilize the RS. The RS solution obtained was added 8 mL of 1.2 M sodium acetate buffer (pH 3.8). After incubation with amyloglucosidase (0.1 mL, 3300 U/mL) at 50 °C for 30 min, the samples were centrifuged at 1500 × g for 10 min. Three milliliters of GOPOD was added to aliquots (0.1 mL) of the supernatant, and the mixture was incubated at 50 °C for 20 min. Absorbance was measured using a spectrophotometer at 510 nm.

2.5. Determination of DS

DS is the average number of hydroxyl groups substituted per glucose unit. Due to the reaction of CA and Cu^{2+} could form a stable complex, Klaushofer et al. (1979) utilized this property to determine the DS of CA-starch by titrating with copper sulfate solution.

However, the above-mentioned method consumes more time and has poor stability. Therefore, in our present study, the DS of CA-starch was determined using a titration method (Kweon, Choi, Kim, & Lim, 2001). The CA-starch (5.0 g, dry basis) was weighed accurately and dispersed with 50 mL distilled water in a conical flask. Subsequently, phenolphthalein solution (1%, w/w) was added as an indicator. The suspension was adjusted to be a reddish solution, and then 25 mL of NaOH (2.5 M) was added into the flask by stirring for 60 min. The starch solution was titrated with 0.5 M standard HCl solution. The native starch is used as a control. The DS was calculated by using the equation.

$$A\% = \frac{(V_0 - V_1) \times M \times 0.158 \times 100}{W} \quad (1)$$

$$DS = \frac{162 \times A}{15800 - 156 \times A} \quad (2)$$

Where A is CA substitutions (%), M is the standard molarity of HCl solution, W is the weight of starch, 158 is the molecular weight of CA, 162 is the relative molecular mass of starch, DS is the degree of substitution.