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Effect of the phytate and hydrogen peroxide chemical modifications on the physicochemical and functional properties of wheat starch

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ABSTRACT

To investigate the characteristics of chemically modified wheat starch, such as oxidized (OWS), cross-linked (CLWS) and dual-modified wheat starches, cross-linked oxidized (COWS) and oxidized cross-linked (OCWS) wheat starches were obtained by 12% hydrogen peroxide (H_2O_2) and 2% sodium phytate treatments, respectively. After modifications of wheat starch by cross-linking and oxidization, it was determined that native wheat starch was effectively modified with respect to the structure and physicochemical characteristics, as detected by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), Rapid Visco Analyzer (RVA), scanning electron microscopy (SEM) and X-ray diffraction (XRD). DSC analysis demonstrated that peak temperature (T_p) 64.41 °C of the COWS was the highest. The RVA viscosity indexes of CLWS were noticeably increased compared with the other four starches, of which three oxidized starch samples showed lower RVA profiles because of oxidation. The XRD result indicated that cross-linked phosphates from sodium phytate were primarily located in the amorphous regions of starch granules. After modifications by different treatments, the starch samples exhibited different morphological characteristics, including A-type and B-type wheat starch granules, which showed much closer contact with each other by the cross-linking reaction under SEM observations. The functional characteristics, including solubility, swelling power, light transmittance and freeze-thaw stability (FTS), of all five treated and untreated wheat starches demonstrated that COWS had the highest solubility at 0.57 and that CLWS showed the best swelling power at 12.63 (g/g). The paste clarity of COWS was improved to 47.72% higher than that of native starch (7.54%), and the water loss of COWS (21.62%) was the lowest, which is beneficial to the production of quick-frozen food. Our results showed that dual-modified starch by using sodium phytate and hydrogen peroxide had significantly altered structural and functional properties. The present study provides fundamental information of dual-modified wheat starch for its potential industrial application.

1. Introduction

As one of the important cereal crops, wheat is cultivated worldwide to provide proteins and starches for human beings and to supply forage for livestock (Shewry, 2009). Wheat starch, accounting for 75% of the wheat grain weight, is also the main reproducible and biodegradable polymeric carbohydrate supplier (Miskelly, Batey, Suter, Wrigley, & Batey, 2010; Singh, Singh, Isono, & Noda, 2010; Wang et al., 2014). To date, starches have been applied in food manufacturing widely as a gel stabilizer, gelatinizer, densifier, water holder and raising agent for a long time (Tharanathan, 2005; Wang & Copeland, 2013). However, native starches have low light transmittance, poor freeze-thaw stability, sensitivity to excessive pH conditions and high tendency for retrogradation, which limit the applications of native starches both in modern food and non-food processing industries (Witczak, Juszczak, Ziobro, & Korus, 2012; Xiao, Lin, Liu, & Yu, 2012).To overcome these shortcomings and obtain new better physicochemical performance and functional characteristics, starch modifications using chemical, physical, genetic and enzymatic methods must be applied (Copeland, Blazek, Salman, & Tang, 2009; Sahnoun, Ismail,- & Kammoun, 2016; Singh, Kaur, & McCarthy, 2007).

The chemical procedures may be the most classical and effective methods for starch modification, such as oxidized, cross-linked, etherified, hydroxypropylated, and acetylated modified starches (Fornal et al., 2012; Masina et al., 2016; Sukhija, Singh, & Riar, 2016). Chemical modification such as oxidized and cross-linked reactions can consequently alter starch gelatinization, the thermal properties, and pasting performance by

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introducing functional units into the starch molecules (Kaur, Singh,- & Singh, 2004; Maulani, Fardiaz, Kusnandar, & Sunarti, 2013; Singh et al., 2007). The oxidized starches have been widely used in both food and industrial applications to provide film product and adhesion characteristics in recent times (Sukhija et al., 2016). Moreover, cross-linking reaction can add chemical bonds at the location in starch granules and stabilize the granules and reinforce the relatively tender starch, resulting in better resistance to acid, heat and shearing, higher viscous and reduction in the tendency to solubilize and rupture (Kaur, Singh, & Singh, 2006). Phytic acid is a natural antioxidant with six hydrophilic phosphate groups and has been widely used in the pharmaceutical, food, and cosmetic industries (Landoni et al., 2013; Lott, Ockenden, Raboy, & Batten, 2000). However, there is no documented research about modified wheat starch using sodium phytate and composite modified wheat starch using by sodium phytate and hydrogen peroxide until now. Additionally, the composite modified starch can offset the deficient characteristics, and it can exhibit better properties and more comprehensive applications compared with the single modification (Hirao, Nagata, Naito, Sorimachi, &- Takahashi, 2005; Zhou, Meng, Chen, Zhu, & Yuan, 2014).

In the present study, we aimed to produce the dual-modified wheat starches using hydrogen peroxide and sodium phytate treatments and investigate the physicochemical properties and mechanism of action preliminarily. Using FTIR, XRD, DSC and RVA, we compared the physicochemical and functional characteristics of native, oxidized, cross-linked, cross-linked oxidized and oxidized cross-linked wheat starches, as well as paste clarity, swelling power and freeze-thaw stability. Our results showed that dual-modified starch by using sodium phytate and hydrogen peroxide had significantly altered structural and functional properties.

2. Materials and methods

2.1. Materials

The native wheat starch sample (NWS) was prepared from Zhengmai 9023 (*Triticum aestivum* L.) which was planted in the HUST experimental field (Wuhan, China). The method used to isolate starch from wheat flour was the dough ball method (Finnie, Jeannotte, Morris, Giroux, & Faubion, 2010). The hydrogen peroxide (product no. 10011218, CAS no. 7722-84-1) and sodium phytate (product no. SP881002, CAS no. 14306-25-3) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, and all the reagents we used were of analytical grade.

2.2. Synthesis of cross-linked wheat starch

Cross-linked starch (CLWS) was prepared using the protocol of Yoon, Thompson, and Jenkins (1983) with some modifications and was based on single-factor experiments with respect to the dosage of sodium phytate, pH value, reaction time, reaction temperature, and concentration of starch. The phosphorous content of the native and chemically modified wheat starch samples was determined according to methods described in the literature (Noda et al., 2004). Briefly, wheat starch (30 g) was added to 70 ml of distilled water. The 2% sodium phytate on a dry basis (db) was added to the starch slurry, followed by stirring at 200 rpm for 6 h at 50 °C in an incubator with constant temperature and the pH adjusted to 7 with 0.1 mol/L hydrochloric acid. Thereafter, the modified wheat starch was isolated by centrifuging the starch slurry (3, 500 rpm, 960 g, 15 min), and sediment was washed with deionized water. The process was terminated when the supernatant showed no response to $AgNO_3$ solution. The sediment was dried at − 50 °C for 24 h in a vacuum freeze-drying oven (FD-1A-50, Boyikang, Beijing, China). The possible chemical reaction equation for cross-linked starch with sodium phytate is shown in Fig. 1(A).

2.3. Synthesis of oxidized wheat starch

Oxidized starch (OWS) was obtained according to the document presented by Sangseethong, Termvejsayanon, and Sriroth (2010). Wheat starch slurry (40%) was prepared by use of the conical flask and adjusted the pH to 8.0 with 1 M NaOH. Ferrous sulfate ($FeSO_4$) was added into the slurry maintained at 45 °C as catalyst (0.07% based on dry starch basis) and then H_2O_2 solution was added to the starch mixture dropwise within 15 min to reach a 12% terminal concentration (Guidotti et al., 2011). The above-mentioned process was maintained for three hours at the same pH value and temperature in a constant temperature incubator. Then the slurry was adjusted pH to 6.5 to terminate reaction using 1 M hydrochloric acid (HCL). OWS was obtained after the slurry was centrifugated (3500 rpm, 960 g, 20 min). Sediment was washed with ultrapure water thoroughly. The reaction was terminated when the supernatant showed no response to $AgNO_3$ solution and starch was dried at − 50 °C for 24 h in a vacuum freeze-drying oven (FD-1A-50, Boyikang, Beijing, China). The possible chemical reaction equation for oxidized starch with hydrogen peroxide is shown in Fig. 1(B).

2.4. Synthesis of dual-modified wheat starches

The COWS and OCWS starch samples were prepared using the methods as mentioned above for cross-linking and oxidation alternatively. The moisture content of five types of starch samples was determined according to the International Association for Cereal Chemistry standard no.110/1 (ICC, 1976).

2.5. Detection of the oxidation degree

The total contents of carbonyl groups and carboxyl groups of the oxidized starches were determined by a simple method based on the protocol by Zhang, Wang, Zhao, and Wang (2012). Dry base starch (100 mg) was mixed with distilled water (50 ml) and then 10 ml of 0.1 M NaOH solution was added. After mixing thoroughly, the slurry was heated for 20 min at 100 °C to ensure complete solubilization. After cooling to normal room temperature, the solution was adjusted to a pH lower than 7.0 with 0.2 M hydrochloric acid. Thereafter, the slurry was maintained to boil for 1 min again and was back titrated rapidly with 0.10 M sodium hydroxide to the phenolphthalein end-point. Native starch was achieved as a blank control, and all specimens were measured three times to determine the values using the Formulas (1) and (2) below.

$$DO = \frac{C_{NaOH}V_{NaOH} - C_{HCl}V_{HCl}}{m/162} \times 100\% \quad (1)$$

$$DO_S = DO_M - DO_N \quad (2)$$

where C_{NaOH} and C_{HCl} stand as the concentrations of NaOH and HCl solutions, respectively. V_{NaOH} and V_{HCl} were the total volumes of consumed NaOH and HCl solutions. m represents the weight of dry starch. The DO of the samples was shorted as DO_S, The DO of the measured modified starch was shorted as DO_M and DO of the native starch was shorted as DO_N.

2.6. Measurements of starch solubility, swelling power and paste clarity

The solubility and swelling power (SP) of starch samples were measured as described by Lee and Yoo (2011). The ground starch (40 mg, dry base, db) was resuspended in 4 ml of ultrapure water in the tubes covered with screw caps. The slurry was stirred for 1 h with moderate vortex mixing at 25 °C moderately. Next it was maintained at 90 °C for 30 min. Thereafter, the slurry was cooled to normal room temperature quickly and centrifuged at 3500 rpm, 960 g for 15 min. Supernatant was moved into another container and was dried at 70 °C