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The influence of ultrasound on the degree of oxidation of hypochlorite-oxidized corn starch

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ABSTRACT

Oxidized corn starch was prepared with and without sonication at different levels of sodium hypochlorite (0–2 g active chlorine/50 g starch) and treatment time (15 and 30 min). Gel permeation chromatography revealed that weight average molecular weight decreased while polydispersity index increased with increase in active chlorine concentration and treatment time. It was found that carbonyl and carboxyl contents, and swelling power of oxidized corn starch generally increased with progressive increase in active chlorine level, treatment time and in the presence of sonication. A reversed trend was observed for the solubility. Peak viscosity was found to decrease with increase in active chlorine concentration to a threshold level of 1 g active chlorine/50 g starch, after which peak viscosity increased as the active chlorine level was increased. Breakdown values and final viscosities were increased and decreased respectively with progressive increase in active chlorine concentration. These phenomena became significant as the starch was subjected to sonication and longer treatment time.

1. Introduction

Starch is the main source of energy for humans (Miyazaki, Hung, Maeda, & Morita, 2006). Native starch has been used in various food preparations primarily based on its thickening or binding properties (Jobling, 2004; Rengsutthi & Charoenrein, 2011). The limitation in usage is due to the fact that native starch shows poor tolerance to a broad range of processing conditions and poor functional properties (Thomas & Atwell, 1999). However, these shortcomings can be overcome through chemical or enzyme modification, and physical treatment and this has made starch becomes a useful polymer in industrial applications as modification can enhance starch positive attributes and/or to overcome the inconsistency of starches (Jobling, 2004).

One of the common chemical modifications of starch is oxidation. Oxidized starch shows lower viscosity at high solid content, lower retrogradation property, better clarity, film forming and binding properties than the native ones. All these have diversified starch applications in food and non-food industries. In food applications, oxidized starch is used in batters and breading, as fillings in bakery products (Kuakpetoon & Wang, 2001; Thomas & Atwell, 1999).

The common oxidants used to produce oxidized starch are permanganate (Takizawa, Silva, Konkel, & Demiate, 2004), hydrogen peroxide, hypochlorite (Sangseethong, Termvejsayanon, & Sriroth, 2010) and oxygen (Ye et al., 2011), Among the abovementioned, sodium hypochlorite is the most popular used oxidizing agent for producing oxidized starches at commercial level (Kuakpetoon & Wang, 2001). According to Wurzburg (1986), there are two major reactions taking place during starch oxidation. The first reaction occurs mainly on the hydroxyl groups at the C-2, C-3 and C-6 positions of D-glucopyranosyl with these hydroxyl groups being oxidized to carbonyl groups and then to carboxyl groups. The second reaction is the depolymerization of starch molecules by primarily hydrolyzing amylose and amylopectin molecules at α-D-(1 → 4) glycosidic linkages. Hence, the carbonyl and carboxyl contents as well as the degree of degradation are generally used to indicate the extent of starch oxidation. The degree of hypochlorite oxidation is affected by many factors such as starch molecular structure, starch origin, packing of crystalline lamellae and the size of amorphous lamellae, pH, temperature, concentration of oxidants and catalyst (Kuakpetoon & Wang, 2001; Tolvanen, Mäki-Arvela, Sorokin, Salmi, & Murzin, 2009; Wang & Wang, 2003; Wurzburg, 1986).

The application of ultrasonic irradiation in food processing has been increasing from the past few years because it shortens the processing times required and it also lowers the energy consumption, making it an effective process (Jambrak, Lelas, Mason, Krešić, & Badanjak, 2009; Mason, Paniwnyk, & Lorimer, 1996). When liquid is irradiated with high intensity ultrasound, microbubbles are formed, with dissolved gas acting as the nucleic. These microbubbles oscillate, grow into slightly larger size during

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the expansion cycle then shrink during the compression cycle. Once reaching a critical size called the resonant size, the microbubbles will eventually implode violently and generates very high pressure and temperature which lead to production of very high shear energy waves and turbulence. This process is called the cavitation (Leighton, 1994; Mason & Lorimer, 2002; Suslick, 1994). The power ultrasound through cavitation can cause drastic changes in chemical, functional and physical properties of solute present in the liquid medium (Jambrak et al., 2009).

Zuo, Knoerzer, Mawson, Kentish, and Ashokkumar (2009) studied the pasting behaviour of sonicated waxy rice starch suspensions. They found that the length of sonication time and the solution temperature markedly influenced the functionality of starch granules. Recent study by Jambrak et al. (2010) on the effect of ultrasound on physical properties of corn starch reported that ultrasound irradiation ruptured and mechanically disrupted the starch granules. In short, the results of previous works have showed that sonication does affect the physicochemical properties of starch in different manners such as degradation, solubilization and swelling.

The aim of this work was to investigate the effect of sonication on the degree of oxidation of oxidized corn starch produced with different levels of sodium hypochlorite (NaOCl).

2. Materials and methods

2.1. Materials

Commercial corn starch containing 26.47 g amylose/100 g was purchased from Sim Company Sdn. Bhd, Penang, Malaysia. Sodium hypochlorite (NaOCl) containing 10 g active chlorine/100 g was used in this experiment. All other chemicals used were of analytical grade.

2.2. Sample preparation

Corn starch slurry was prepared by dispersing 50 g of starch in 450 g of deionized water. The starch slurry was maintained at 35 °C in a water bath and pH was adjusted to 9–10 with 2 mol equivalent/L NaOH with consistent stirring using an overhead stirrer. Active chlorine content was adjusted to 0.06–2 g/50 g starch in 30 min while maintaining the pH at 9–10 with 0.5 mol equivalent/L H_2SO_4. Sonication was carried out in an ultrasonic bath (Transsonic TI-H-10, Elma, Germany) with power ultrasound of 200 W with 100% amplitude at a frequency of 25 kHz and the intensity was 13 W cm^{-2}. Sonication was continued for 15 min or 30 min under continuous stirring to prevent the starch granules from settle to the bottom. After which, the starch slurry was adjusted to pH 7.0 with 0.5 mol equivalent/L H_2SO_4; vacuum filtered, washed with deionized water, washed with absolute ethanol and dried in a vacuum oven at 30 °C overnight. Parallel control of these five level hypochlorite-oxidized corn starches were also prepared by employing the same procedure with only stirring for 15 min and 30 min without sonication. Control samples were also prepared by applying same conditions as oxidized starch without any hypochlorite addition.

2.3. Gel permeation chromatography

The weight average molecular weight (M_w) and polydispersity of unmodified and modified starches were determined using a Malvern Viscotek Triple Detection GPCMax (Light Scattering Detector, RI Detector and Viscometer) gel permeation chromatography (GPC) system which consisting of an inline eluent degasser, a syringe-loading sample injector equipped with a 100 μL sample loop and dual linear (connected in series) Viscotek A6000M Aqueous GPC/SEC column packed with hydroxymethacrylate polymer. The mobile phase was an aqueous solution of 0.1 mol equivalent/L $NaNO_3$ at a flow rate of 1.0 mL/min. Starch sample (0.1 g) was prepared in dimethyl sulphoxide (DMSO), shoke for 1 h in a 95 °C water bath, and was then stirred at room temperature for 24 h. An aliquot (1.5 mL) was taken and added with 6 mL of absolute alcohol. The precipitated starch was recovered by centrifugation at 2000*g* for 30 min and washed twice with ethanol by centrifugation for 15 min to remove dimethyl sulphoxide (DMSO). Then, the precipitated starch was redissolved in 5 mL deionized water by stirring for 30 min in a heating water bath. The mixture was then centrifuged at 2000*g* for 15 min to remove insoluble residue prior to injection.

2.4. Carbonyl and carboxyl contents determination

Carbonyl and carboxyl contents of native and modified corn starch samples were determined according to the titrimetric method of Kuakpetoon and Wang (2006).

2.5. Swelling power and solubility determination

Swelling power and solubility of starch samples were determined in quadruplicates as described by Chan, Bhat, and Karim (2010).

2.6. Pasting properties

The pasting properties of starch were evaluated in quadruplicates according to the method of Chan et al. (2010) using a Rapid Visco-Analyzer (RVA) (Model RVA-4; Newport Scientific Pvt. Ltd., Warriewood, Australia) and software program Thermocline for Windows (TCW). The viscosity was measured in Centipoise (Cp).

2.7. Statistical analysis

The data reported were averages of quadruplicate observations. The data were subjected to statistical analysis using SPSS 14.0 (SPSS Inc., Chicago, USA). One-way analysis of variance (ANOVA) was performed. Duncan's multiple range test ($p < 0.05$) was carried out to evaluate significant differences between means.

3. Results and discussion

3.1. Gel permeation chromatography

The weight average molecular weight (M_w) and polydispersity index of samples prepared are tabulated in Table 1. Results show that corn starch subjected to modification exhibited a marked difference in molecular mass properties compared to the unmodified counterpart. Starch subjected to sonication only shows higher M_w value, whereas the M_w values of oxidized and soni-oxidized starches are lower as compared to the native starch. The M_w values of oxidized samples decreased with active chlorine content and treatment time. The lower M_w could be attributable to depolymerization of starch molecules, i.e. amylopectin and amylose chains during the modification process. This observation is consistent with the study of Wang and Wang (2003), who reported that the degree of starch molecules degradation increased with oxidant concentration. It is noted that at a specific active chlorine level, greater depolymerization was evident with the use of sonication. The increase in M_w for sonicated starch was unexpected and the plausible explanation could be intermolecular crosslinks formed between the functional groups. However, further analysis is needed to substantiate this explanation.

Polydispersity index (M_w/M_n) is generally used as an indicator of the broadness of a molecular weight distribution of a polymer.