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Effect of deproteinization on degree of oxidation of ozonated starch

Hui-Tin Chan [a], Ariffin Fazilah [a], Rajeev Bhat [a], Chiu-Peng Leh [b], Alias A. Karim [a,*]

[a] Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[b] Bioresource, Paper & Coatings Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

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ABSTRACT

Effects of deproteinization on the degree of oxidation of ozonated starch (corn, sago, and tapioca) were investigated. Starch in dry powder form was exposed to ozone for 10 min at different ozone generation times (OGTs: 1, 3, 5, 10 min), and then native starches (NS) and deproteinized starches (DPS) were analyzed for protein content. Deproteinization caused a significant reduction in protein content for corn (~21%) and sago (~16%) starches relative to NS. Carbonyl and carboxyl contents increased significantly in all ozonated deproteinized starches (ODPS) with increasing OGT. Carbonyl and carboxyl contents of ODPS ranged from 0.03 to 0.13% and 0.14 to 0.28%, respectively. The carboxyl content for all ODPS was significantly higher than that of ozonated native starches (ONS). A Rapid Visco Analyser was used to analyze pasting properties of all starches. Deproteinization increased the pasting viscosities of corn and sago starches compared to their native forms. Generally, pasting viscosity of all ODPS decreased drastically as OGT increased. At the highest oxidation level (10 min OGT), all ODPS exhibited the lowest pasting viscosities compared to their ozonated native form, except for peak viscosity, breakdown viscosity, and setback viscosity for ozonated deproteinized corn starch. In conclusion, deproteinization as a pretreatment prior to starch ozonation successfully increased the degree of oxidation in the three types of starch studied. However, the extent of starch oxidation varied among the different starches, possibly due to differences in rates of degradation on amorphous and crystalline lamellae and in rates of oxidation of carbonyl and carboxyl groups.

1. Introduction

Starch is a mixture of two polysaccharides: the linear molecule of amylose and a highly branched molecule of amylopectin. Starch is widely used in the food, paper, and textile industries. However, the uses of native starches are limited by some undesirable properties. Therefore, starches must be modified chemically, physically, genetically, or enzymatically to enhance their positive attributes or to minimize their defects. In the paper, textile, and building material industries, oxidized starch is widely used to provide surface sizing and coating properties (Chang, Park, Shin, Suh, & Kim, 2008). In the food industry, the use of oxidized starch has become increasing important because it has low viscosity and good binding and film forming properties (Kuakpetoon & Wang, 2006).

Oxidized starch is produced by reacting starch with a specified amount of oxidizing reagent under controlled temperature and pH (Wurzburg, 1986). Sodium hypochlorite is the most common chemical oxidizing agent used to study starch oxidation. However, in the hypochlorite oxidation process, the oxidized starch yield is low because small molecules are lost due to starch breakdown (Wing & Willett, 1997). In addition, a large amount of waste water is produced during the process of oxidation (Kesselmans & Bleeker, 1997a). Ozone is a more powerful oxidant than oxygen, it reacts with most substances at ambient temperatures, and it creates no waste water disposal problem. Furthermore, a dry process using ozone can reduce the purification cost and produce a product with high recovery. Several patents have been filed for a method of oxidizing dry starch (Kesselmans & Bleeker, 1997a) and polysaccharides (Kesselmans & Bleeker, 1997b) using ozone as an oxidizing agent. In addition, some recent scientific publications have reported the use of ozone in starch modification. An and King (2009) reported that ozonated rice starch exhibited similar pasting properties to those from oxidized starches treated with low concentrations of chemical oxidizing agents. On the other hand, Lii, Liao, Stobinski, and Tomasik (2003) reported that the corona discharge method used discharges decomposed starches to low molecular fragments together with oxidation of the polysaccharides. Our previous study (Chan, Bhat, & Karim, 2009) demonstrated that ozone gas successfully oxidized starches from a variety of different starches. However, the degree of oxidation in

* Corresponding author. Tel.: +60 4 653 2268; fax: +60 4 657 3678.
E-mail address: akarim@usm.my (A.A. Karim).

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terms of total carboxyl content was lower than that reported in the literature. Therefore, we postulated that if the ozone gas has more access to the interior or subsurface of the starch granule, a higher degree of oxidation would occur.

In addition to amylose and amylopectin, starch granules contain minimal quantities of components like protein, lipids, and minerals (Morrison, 1995). Starch granule associated proteins (SGAPs) are defined as the proteins naturally positioned in and on starch granules (Baldwin, 2001).The presence of protein in/on starch granules might influence the starch's physicochemical properties, such as swelling, solubility, and gelatinization temperature (Shull, Chandrashekar, Kirleis, & Ejeta, 1990; Tester & Morrison, 1990). The presence of surface material on the granule acts as the first barrier to processes such as granule hydration, enzyme attack, and chemical reaction with modifying agents. Therefore, we postulated that removal of these surface materials might increase the extent of chemical reactions with the modifying agent. Eerlingen, Cillen, and Delcour (1994) reported that sodium dodecyl sulfate (SDS) treatment can efficiently remove the surface protein from starch granules. We previously reported a significant reduction in protein content for all starches studied after treatment with 0.2% SDS solvent compared with the starches in their native form (Chan, Bhat, & Karim, 2010).

This study was designed to explore the effect of deproteinization on starches in greater detail. The objectives of this study were to investigate the effect of deproteinization on the degree of oxidation of ozonated starch and to determine the effect of these treatments on the pasting properties of the treated starch.

2. Materials and methods

2.1. Materials

Corn, potato, and sago starch were purchased from the Sims Company Sdn. Bhd (Penang, Malaysia). All other reagents used in this work were of analytical grade. All native starches and chemicals were used directly without further purification.

2.2. Sodium dodecyl sulfate (SDS) treatment

Starch (40% w/v) was suspended in SDS solvent (2% w/v) at room temperature. The starch suspension was stirred for 30 min using a magnetic stirrer and then centrifuged (Kubota 5100, Kubota Corp., Tokyo, Japan) at 3500 rpm for 15 min. The supernatant was carefully removed. The pellet was washed three times, re-suspended with distilled water, centrifuged, and dried in an oven at 40 °C for 12 h. Duplicate samples from each type of starch were prepared and used for ozone oxidation.

2.3. Preparation of ozone-oxidized starches

Oxidized-native and SDS-treated corn, sago, and tapioca starches were prepared by a method originally described in Chan et al. (2009). Briefly, a starch sample in powder form ("as is" moisture content) was placed in a reaction vessel that was connected to an ozone (O_3) generator. O_3 was generated for 1 min, 3 min, 5 min, and 10 min (i.e., oxygen generation times, OGTs) and the reaction vessel was rotated at 150 rpm to ensure homogeneous contact between starch and O_3 during the reaction. Following the specified OGT, 10 min of contact time elapsed with both the gas inlet and outlet closed to allow the oxidation reaction to take place. Finally, O_2 was flushed through the vessel for 20 min to flush out the O_3 that did not react with the starch. When this process was completed, the oxidized starch was collected and analyzed. Duplicate samples for each OGT were prepared for each starch type.

2.4. Protein content analysis

Protein content of native starch (NS) and deproteinized starches (DPS) was determined using the macro-Kjeldahl method (AOAC, 1990). The crude protein content on a wet basis was calculated by multiplying nitrogen content by a factor of 6.25. Each starch was analyzed in duplicate and the protein content was reported as the percent of protein.

2.5. Carbonyl content (%)

The carbonyl group content for ONS and ODPS was determined following the titrimetric method of Smith (1967). The carbonyl group content was calculated as follows:

$$\text{Percentage of carbonyl content} = [(\text{blank} - \text{sample})\ \text{mL} \times \text{acid normality} \times 0.028 \times 100]/\text{sample weight (dry basis) in g} \quad (1)$$

2.6. Carboxyl content (%)

The carboxyl content of ONS and ODPS was determined according to the modified procedure of Chattopadhyay, Singhal, and Kulkarni (1997). A starch sample (2 g) was mixed with 25 mL of 0.1 M HCl, and the slurry was stirred continuously for 30 min with a magnetic stirrer. The slurry then was vacuum filtered through a 150 mL medium porosity fritted glass funnel and washed with 400 mL of distilled water. The starch cake was carefully transferred into a 500 mL beaker, and the volume was adjusted to 300 mL with distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. The hot starch dispersion was then adjusted to 450 mL with distilled water and titrated to pH 8.3 with standardized 0.01 M NaOH. A blank test was performed with unmodified starch. The carboxyl content was calculated as follows:

$$\text{Milliequivalents of acidity/100 g starch} = [(\text{sample} - \text{blank})\ \text{mL} \times \text{normality of NaOH} \times 100]/\text{sample weight (dry basis) in g} \quad (2)$$

$$\text{Percentage of carboxyl content} = [\text{milliequivalents of acidity/100 g starch}] \times 0.045 \quad (3)$$

2.7. Pasting properties of starch

The pasting profile of the starches (12% w/w) was determined using a Rapid Visco™ Analyser (Model RVA-4, Newport Scientific Pvt. Ltd., Warriewood, Australia). The samples were equilibrated at 50 °C for 1 min and then increased to 95 °C in 3.75 min, held for 2.5 min, cooled to 50 °C in 3.75 min, and held for 5 min. The paddle speed was set at 960 rpm for the first 10 s to consistently disperse the starch slurry and then it was reduced to 160 rpm throughout the remainder of the experiment. The units of viscosity were expressed as Rapid Visco Units (RVUs).

2.8. Statistical analysis

The starch type (ONS or ODPS) and OGTs were two factors that were analyzed by analysis of variance (ANOVA) using SPSS 15.0 software (SPSS, Inc., Chicago, IL, USA). Duncan's least significant test was used to compare means at the 5% significance level. Type of