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Locations of hypochlorite oxidation in corn starches varying in amylose content

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Abstract—The general oxidation mechanism by hypochlorite on starch has been well studied, but the information on the distribution of the oxidation sites within starch granules is limited. This study investigated the locations where the oxidation occurred within corn starch granules varying in amylose content, including waxy corn starch (WC), common corn starch (CC), and 50% and 70% high-amylose corn starch (AMC). Oxidized corn starches were surface gelatinized by 13 M LiCl at room temperature to different extents (approximately 10%, 20%, 30%, and 40%). The surface-gelatinized remaining granules were separated and studied for structural characteristics including carboxyl content, amylose content, amylopectin chain-length distribution, thermal properties, and swelling properties. Oxidation occurred mostly at the amorphous lamellae. More carboxyl groups were found at the periphery than at the core of starch granules, which was more pronounced in oxidized 70% AMC. More amylose depolymerization from oxidation occurred at the periphery of CC. For WC and CC, amylopectin long chains (>DP 36) were more prone to depolymerization by oxidation. The gelatinization properties as measured by differential scanning calorimetry also supported the changes in amylopectin fine structure from oxidation. Oxidized starches swelled to a greater extent than their unmodified counterparts at all levels of surface removal. This study demonstrates that the locations of oxidation and physicochemical properties of oxidized starches are affected by the molecular arrangement within starch granules.

Keywords: Oxidized starch; Hypochlorite; Carboxyl; Carbonyl; Amylopectin chain-length distribution; Amylose content; Starch structure; High-amylose corn starch; Surface gelatinization

1. Introduction

Oxidized starch is commonly produced by reacting starch with a specified amount of NaOCl under controlled temperature and pH.[1] There are two main reactions involved in oxidation. Firstly, hydroxyl groups in starch molecules are oxidized to carbonyl groups and then to carboxyl groups, which primarily takes place at C-2, C-3, and C-6.[1] Secondly, oxidation also causes depolymerization of starch molecules by cleaving α-(1→4)-glucosidic linkages.[1] Therefore, carboxyl and carbonyl content and/or extent of depolymerization in oxidized starches could indicate oxidation efficiency.

Oxidation efficiency can be affected by many factors, including pH, temperature, hypochlorite concentration, starch molecular structure, and starch organization.[1–8] Our previous study[8] showed that potato starch was much more prone to oxidation than were corn and rice starches under the same oxidation conditions. The loose arrangement of B-type crystalline structure[9,10] in potato starch may provide more accessible sites for oxidation.

Hypochlorite could be consumed during starch oxidation by three possible mechanisms: namely, lipid oxidation, depolymerization of amylose and amylopectin, and formation of carboxyl and carbonyl groups.[11] Significant differences in oxidation efficiency were observed among corn starches with varying amylose content when they were oxidized under the same conditions.[11] Hypochlorite was suggested to first react with lipid,

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presumably from an amylose–lipid complex, and then either to depolymerize the starch molecule or form carboxyl and carbonyl groups. More hypochlorite was consumed for depolymerization of starches containing more amylose and amylopectin long chains such as in high-amylose corn starch. In contrast, more carboxyl formation was observed for starches low in amylose as in waxy corn starch. Amylopectin was more prone to carboxyl formation than was amylose.

Previous work[12,13] has shown non-uniformly distribution of amylose and amylopectin along the radial location within starch granules. Amylose was found to be more concentrated at the periphery, and more amylopectin long-B chains were at the core in common corn starch.[12] This radial dependence of molecular distribution was also recently confirmed and suggested to be influenced by starch composition.[14] The objectives of this study were to investigate the distribution of oxidation sites along the radial locations within corn starch granules varying in amylose content by using chemical surface gelatinization, and to characterize the structure and physicochemical properties of the remaining oxidized corn starches after different degrees of surface removal.

2. Results and discussion

2.1. Birefringence and morphology of starch samples

The polarized light micrographs of hypochlorite-oxidized waxy corn starch (WC), common corn starch (CC), 50% amylose corn starch (50% AMC), 70% amylose starch corn (70% AMC), and their remaining

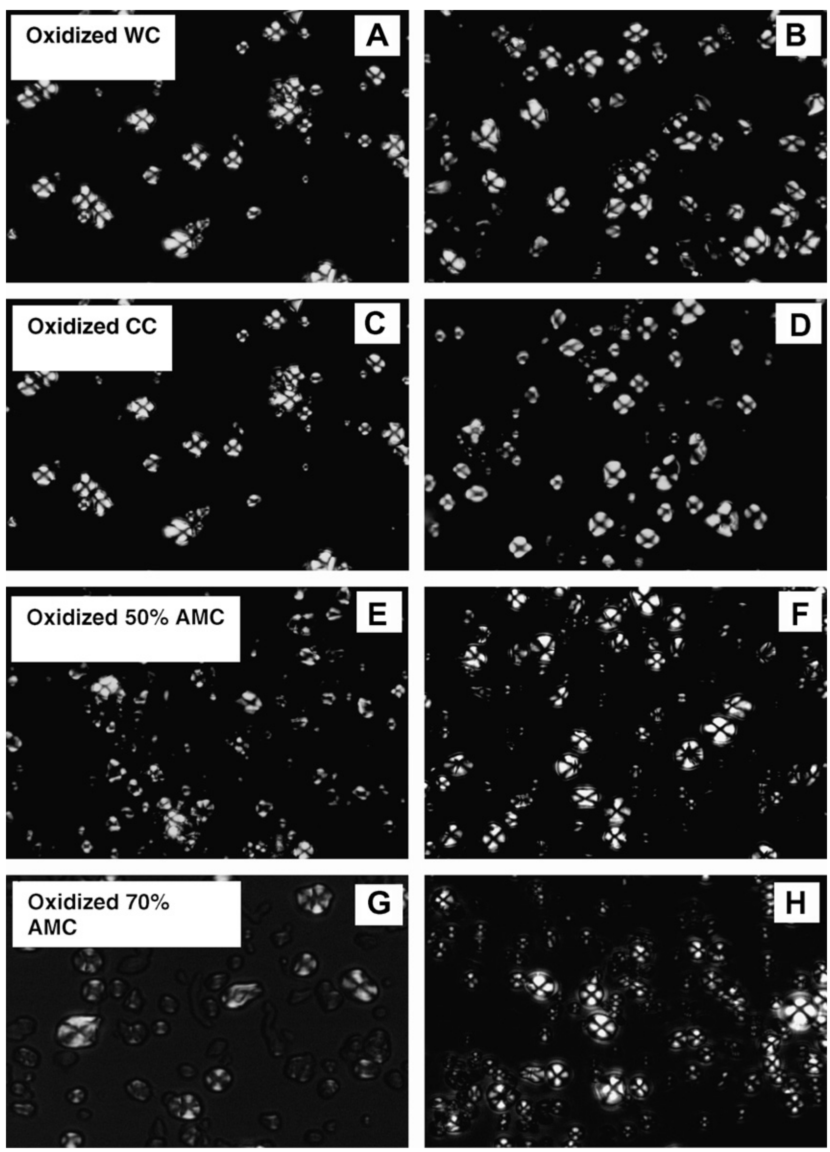

Figure 1. Polarized light micrographs of oxidized starches (A, C, E, G) and their remaining granules after ~40% surface gelatinization (B, D, F, H).