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# Oxidized and acid thinned starch derivatives of hybrid maize: functional characteristics, wide-angle X-ray diffractometry and thermal properties

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**Abstract**

Starch isolated from hybrid maize (8535-23) was subjected to oxidation and acid thinning. Proximate analyses revealed that moisture, ash, protein, fat, fibre, and pH reduced after oxidation and acid thinning. Percentage amylose content reduced from 20.42% in native starch to 18.76 and 17.65% in oxidised and acid thinned starch derivatives, respectively. Wide-angle X-ray diffraction patterns indicated strong peaks at 15.9°, 17.2°, 18.8°, and 25.0° $2\theta$. No significant difference was observed between the X-ray pattern of the native and modified starches. Both swelling power and solubility increased with increase in temperature. Oxidation and acid thinning reduced swelling power and increased solubility starch. At all pHs, both oxidation and acid thinning reduced the swelling capacity of the native starch. Oxidation increased water and oil absorption capacity of the native starch, while both hydrophilic and hydrophobic properties reduced following acid thinning. Least gelation concentration reduced in acid thinned starch but increased in oxidised derivative. Pasting temperature ($T_p$), peak viscosity ($P_v$), hot paste viscosity ($H_v$), and viscosity after 30 min holding at 95 °C ($H_{v30}$) reduced following both modifications. However, values for cold paste viscosity ($C_v$) and setback (SB) reduced in oxidised derivative and increased in acid thinned starch. Light transmittance of the starch pastes reduced with increase in storage days, however, reduction was more pronounced in native and acid thinned starches. Onset temperature ($T_o$), peak temperature ($T_p$) and conclusion temperature ($T_c$) of gelatinisation reduced in modified starches compared with native hybrid maize starch. Also, gelatinisation enthalpy reduced after oxidation and acid thinning. Enthalpy of regelatinisation increased as days of storage of starch paste increased.


*Keywords:* Oxidation; Acid thinning; Hybrid maize

## 1. Introduction

The processes of starch modifications and their products have attracted considerable attention because of several practical and potential food and non-food applications of such products. Starch, the major storage polysaccharide in plants is widely used in food, paper, textile and pharmaceutical industries. However, uses of this vital biopolymer are always limited by some undesirable characteristics. Starches modifications have been used to eliminate or reduce these undesirable characteristics.

In recent times, chemical modifications such as acid hydrolysis, oxidation, acetylation, esterification, etherification and cross-linking have attracted so much significance [1–5].

Oxidized starches have wide applications in industries such as paper, where it improves the strength and printability of paper. It also has good application in textile, laundry finishing, building material and food industries. The main application of oxidised starch is in paper and textile industries, however, its use in food industry is increasing because of its low viscosity, high stability, clarity, film forming and binding properties, which has been applied in food coatings,

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sealing agents in confectionery and as emulsifiers [6]. Several methods have been applied to starch oxidation and these include the use of hydrogen peroxide, air [7,8], oxygen, ozone, bromine [9], chromic acid, permanganate and nitrogen dioxide [10] as oxidizing agents. Hypochlorite oxidation is the most common method for production of oxidised starches in industrial scale. Following oxidation, the glycosyl residues become substituted with carboxyl and carbonyl groups to different extent and in different proportions, which depends, to a large extent, on the type of starch and the conditions of the reaction [11]. The number of carboxyl and carbonyl groups on oxidised starch indicate the level of oxidation, which takes place primarily at the hydroxyl groups of C-2, C-3, and C-6 positions [12].

Acid modification has been applied to improve the physicochemical properties of starch, particularly in food industries, where they are used in gum candies. Acid modification allows the starch to be used at a higher solids concentration for quick gelling and it provides gum or jelly with shorter texture and flexible properties [13]. It has also been used extensively in textile and paper industries [14,12]. In acid modification, the hydroxonium ion attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage. Acid modification changes the physicochemical properties of starch without destroying its granule structure. In addition, the physicochemical properties of acid thinned starches differ according to their origin and the conditions of preparation [15]. Acid modification increases gelatinisation temperature and gelatinisation endotherm of starches. Gel strength and solubility of starches also increase following acid modification [16,17].

The aim of the present investigation was to examine the effects of oxidation and acid thinning on the functional and physicochemical properties of a starch prepared from hybrid maize.

## 2. Materials and methods

### 2.1. Materials

Hybrid maize seeds coded: 8535-23 was obtained from maize breeding unit International Institute of Tropical Agriculture, (CGIAR/IITA) Ibadan, Nigeria. All other reagents used in this work were of analytical grade.

### 2.2. Isolation of starch

Winnowed 1 kg maize grains were cracked slightly by a blender before steeping in 10 l 0.02 M solution of $NaHSO_3$ for 28 h at (30 ± 2) °C, after which the steeping solution was discarded and the swollen grains were washed with distilled water. The swollen grains were blended for 30 min using warring blender. (Braun Multimix de luxe MX40, type 2291). The slurry obtained after blending was resuspended in 5 l of distilled water. It was screened, using 75 μm sieve and centrifuged for 30 min at 10,000 × *g* (Type GLC-1 Ivan Sorvall Inc., USA). Starch obtained after centrifugation was reslurried in 2 l distilled water and protein was separated from starch by toluene emulsification. Toluene was added (20 ml) to starch suspension and it was thoroughly mixed for 30 min and allowed to stand for another 2 h. An emulsion layer of denatured protein formed at the interface as toluene and water separated and this emulsion layer was discarded. The process was repeated for the starch slurry until emulsion layer became negligible. The starch slurry was then washed with acetone and air-dried for 24 h at (30 ± 2) °C.

### 2.3. Oxidation

The method described by Forssel et al. [18] was employed with modifications. Starch paste was prepared by dispersing 100 g of starch in 500 ml of distilled water. The pH was adjusted to 9.5 with 2 M NaOH. 10 g of NaOCl were added to the slurry over a period of 30 min, while maintaining pH range of 9–9.5, with constant stirring at (30 ± 2) °C. The pH was controlled with 0.5 M HCl or 0.5 M NaOH. The reaction proceeded for 10 min after addition of NaOCl. After the reaction, the pH was adjusted to 7 with 1 M $H_2SO_4$ and the oxidized starch was filtered, washed four times with distilled water and air-dried at (30 ± 2) °C for 48 h.

### 2.4. Acid thinning

Native starch (100 g) was slurried in 0.15 M HCl (500 ml) and stirred magnetically for 8 h, while maintaining a temperature of 50 °C. The acid modified starch was filtered and the residue obtained was washed four times with distilled water. It was dried in the air for 48 h at (30 ± 2) °C.

### 2.5. Carboxyl and carbonyl contents

Carboxyl content was determined using the method described by Parovuori et al. [7]. Five grams oxidized starch sample were slurried in 25 ml of 0.1 M HCl following that, it was stirred for 40 min. The slurry was filtered through a medium porosity fritted glass crucible and the residue obtained was washed with distilled water until it was free of chloride using silver nitrate test. The chloride-free sample was dispersed in 300 ml of distilled water. The dispersion was heated in a steam bath and stirred continuously until the starch gelatinised. The hot sample was titrated with 0.1 M NaOH to a phenolphthalein end point. To quantify acidity due to other sources, mainly fatty acids complexed with amylose, a blank titre was determined. Five grams of native starch were titrated to provide for a blank value.

$$\text{Percent carboxyl} = \frac{(\text{sample titre} - \text{blank titre})\,(\text{ml}) \times \text{alkali molarity} \times 0.045 \times 100}{\text{sample weight}\,(\text{g})}$$

The hydroxylamine method described by Smith [19] was used for the determination of carbonyl content. Two grams