

## Ultra-Microstructural Features of Perborate Oxidized Starch

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**ABSTRACT:** Ultrafine structures of low, medium, and highly oxidized starches, symbolized as LOS, MOS, and HOS, respectively, were thoroughly investigated. These oxidized starches were obtained by treatment of native starch (NS) with three different concentrations of sodium perborate (SPB). Thus, obtained products were studied with respect to major chemical and fine physical characteristics vis-a-vis these of NS (a) acidic and reduced groups creation along with mode of association, (b) significant increase in solubility, and (c) outstanding decrease in apparent viscosity. Thermogravimetric analysis (TGA) revealed thermal stability of the said substrates follows order: HOS > MOS > LOS > NS. Scanning electron micrographs (SEM) showed polygonal or irregular shape with particle size ranging from 2 to 20  $\mu$ . After oxidation, the starch surface became rough and the edges lost their definiteness completely. In conclusion, SPB is an efficient oxidant to produce oxidized starches with useful characteristics, which advocate them to wide applications in textile sizing and medicinal domains. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40170.

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### INTRODUCTION

Starch is one of the most important biopolymers which have wide-spread applications in different disciplines by virtue of its abundance, biodegradation, renewability, and cost effectiveness.<sup>1–3</sup> It is built up of amylose and amylopectin. While amylose is a linear polymer counts of  $\alpha$ -(1–4) glucose units, amylopectin is a branched polymer of linear  $\alpha$ -(1–4) glucose units with periodic branches of  $\alpha$ -(1–6) linkages.

Starch is characterized by unique thermal properties in addition to high functionality due to the presence of plenty of groups on both amylose and amylopectin. This, indeed, promotes starch utilization in synthesis of medical and industrial products. Nevertheless, native starch (NS) suffers from serious drawbacks, which limit its application.

Of these drawbacks: lack of fluidity, inability to form stable suspension or colloidal systems or easy gelatinization or dispersion in cold water. Most of, not all, these shortcomings are due to the fact that starch structure is highly bonded by physical forces, notably, hydrogen bonding and van der Waals forces. In order to remedy such starch defects, starch is chemically modified<sup>4,5</sup> using different routes as stated in the following paragraph:

Chemical modifications of starch can be induced by subjecting it to oxidation,<sup>6–11</sup> esterification,<sup>12–14</sup> etherification,<sup>15–17</sup> cross-

linking,<sup>18–20</sup> and grafting.<sup>21–24</sup> When starch is treated with an oxidant, it undergoes changes in the molecular structure due to creation of acidic and reducing groups along with glucosidic bond session.<sup>25</sup> The magnitude of such changes relies on nature and concentration of the oxidant and conditions used for oxidation as well as on the botanical origin of starch. At any event, however, the oxidized starches obtained display improved and desirable characteristics required really for promotion of starch utilization.<sup>26,27</sup>

The oxidation of starch is always accompanied by an extensive hydrolysis of glucosidic linkages leading to starch depolymerization.<sup>25,28</sup> As a result of depolymerization, oxidized starches exhibit low viscosities at high solid concentrations, improved clarity and stability as a result of the introduction of functional groups.<sup>25</sup> Many oxidants such as sodium hypochlorite,<sup>29–31</sup> bromine, periodate,<sup>32</sup> permanganate,<sup>33</sup> hydrogen peroxide,<sup>34–37</sup> photoinitiator/UV,<sup>11,37</sup> and ammonium persulfate (APS)<sup>32</sup> have been used for starch oxidation. Needless to say that sodium hypochlorite had been mostly used for industrial production of oxidized starch because of the great efficiency of this oxidant, but it may lead to the formation of toxic chlorinated byproducts.<sup>38,39</sup> This and other reasons pertaining to environment were behind the rejection of sodium hypochlorite and placing it among abandoned chemicals.

A new environmentally friendly method for starch oxidation was developed by deploying a novel efficient process where sodium perborate (SPB) is used as an efficient oxidant.

In theory and practice, SPB is inexpensive and nontoxic oxidizing agent and offers unique advantages as being in a solid form of hydrogen peroxide. Hence, it is an effective source of active oxygen, super oxide, and/or perhydroxyl anions, which are the active species for oxidation; meanwhile, SPB is more advantageous than hydrogen peroxide as it provides better conditions of stability even at elevated temperatures.

According to the literature, no work is published so far pertaining to ultrafine structure of SPB-oxidized starches. It is the aim of current work to fulfill this gap. Thus, research is designed to oxidize starch using three different concentrations of SPB in order to obtain LOS, MOS, and HOS. Thus, obtained oxidized starches are then monitored for the carbonyl content, carboxyl content, solubility, apparent viscosity of the cooked samples at different rates of shear, Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD) pattern, thermogravimetric analysis (TGA) as well as scanning electron microscopical images (SEM).

## MATERIALS AND METHODS

### Materials

Native maize starch (NS) was kindly gifted by the Egyptian Company for Starch and Glucose Manufacture, Cairo, Egypt. It was used as received. SPB tetra hydrate was purchased from Sigma-Aldrich Chemie GmbH, Germany, product number: 71810, Commercial oxidized starch (St-APS) was supplied by Misr Spinning and Weaving Company, El-Mahalla El-Kubra, Egypt. Silver nitrate, sodium chloride, and potassium permanganate were supplied by Sisco Research Laboratory PVT. Co. Hydroxyl amine hydrochloride was purchased from Oxford Lab Chem, India, Cas No: 5470-11-1. Sorbitol was purchased from Marawan group Co. Cairo, Egypt. Phenolphthalein and methyl red was supplied by Fisher Scientific, Egypt.

Sodium hydroxide, sulfuric acid, hydrochloric acid, and absolute ethanol were all of laboratory grade chemicals.

### Methods

**Oxidation of Starch by Sodium Perborate.** Starch slurry was prepared by adding 5 g of NS into 40 mL of distilled water containing different amounts of SPB (0.25, 0.5, and 1 g) under mechanical stirring. The mixture was kept at room temperature for 15 min with moderate stirring. After that, the temperature was raised to 90°C and maintained at this temperature for 60 min under continuous gentle stirring. At this end, the reaction temperature was decreased to 25°C. The oxidized starch was precipitated by dropwise addition of absolute ethanol under constant vigorous mechanical stirring. The obtained product was filtered. The filtrate was subjected to repeated washing with 80/20 ethanol/water to remove the unreacted SPB. The product was dried in an oven for 120 min at 70°C. Then, the dried product was milled into powder. The resultant oxidized starches were nominated as LOS, MOS, and HOS according to the concentration of SPB used, namely, 0.25, 0.5, and 1 g/5 g NS, respectively.

### Characterization of the Oxidized Starches

**Carboxyl and Carbonyl Groups Content Determination.** The acidic<sup>40</sup> and reducing (carbonyl) groups of starch before and after oxidation with SPB was determined according to a method of Wing and Willett.<sup>6,26</sup>

In carbonyl content determination, hydroxylamine reagent was prepared by dissolving 25 g hydroxylamine hydrochloride in 100 mL of 0.5M NaOH. The final volume was then adjusted to 500 mL with distilled water. In a stoppered flask, the starch sample (4 g) was slurried in 100 mL of distilled water. The slurry was gelatinized in a boiling water bath for 20 min, cooled to 40°C, and adjusted to pH 3.2 with 0.1M HCl. 15 mL of hydroxylamine reagent was added. The flask was stoppered and agitated in a water bath at 40°C. After 4 h, the sample was rapidly titrated to pH 3.2 with 0.1M HCl. A blank determination with hydroxylamine reagent was performed in the same manner.

The method used for carboxyl content determination depends on the back titration of the carboxyl groups with a standard HCl solution.<sup>26</sup> Soak about 2 g of the native or oxidized maize starches in a 100 mL of 2% alcoholic HCl (80 mL ethanol : 20 mL water) in a closed bottle for 4 h. Shake well from time to time. Filter the contents of the bottle and wash the alcoholic HCl treated starch thoroughly with a mixture of ethanol and water (80% ethanol : 20% distilled water). Filter again. Repeat the wash filter process till free from Cl<sup>-</sup> (silver nitrate is used as an indicator). The pure NS or oxidized starch is then collected and dried in an oven at 100 ± 5°C. Weight accurately about 0.1 g of the dry pure native or oxidized maize starch and transfer to a 250 mL stoppered conical flask. Add 25 mL of 0.1M NaOH to the content of the conical flask and leave for 4 h with shaking from time to time. Make a blank experiment. Titrate the content of the two conical flasks with a standard HCl solution (0.1M). Phenolphthalein is used as an indicator.

$$\text{COOH content (A)} = \frac{(V_b - V_s) \times M_{\text{HCl}}}{W} \times 100 (\text{meq./100g sample})$$

where  $V_b$  is the volume of HCl consumed by the blank experiment,  $V_s$  is the volume of HCl consumed by the blank sample,  $M_{\text{HCl}}$  is the molarity of HCl, and  $W$  is the weight of the sample.

**Apparent Viscosity of Native and Oxidized Starches.** The apparent viscosity of the samples was measured using programmable Rheometer Brookfield, TC 200 (Model, DV-III, USA). Dry samples of NS or oxidized starches (5 g of starch before and after oxidation) were dispersed in ~90 mL of distilled water and the pH was adjusted to 9.0. The solutions were stirred for 60 min, followed by raising the temperature to 90°C then kept at this temperature for 15 min. The final volume was adjusted to 100 mL and the pH was adjusted to 9.0. The pastes formed were left to cool to 25°C. Viscosities were measured using viscometer with a # 18 spindle at rates of shear (0–250 s<sup>-1</sup>).<sup>6</sup>

**Solubility of Native and Oxidized Starches.** Five grams of NS, LOS, MOS, and HOS were placed in 150 mL of distilled water and the pH was adjusted and maintained at 9.0 under

continuous stirring at 25°C for 60 min. The samples were then filtrated and the recovered solids were collected and oven dried.<sup>6</sup> The solubility measurement was repeated three times for each sample. The solubility was calculated according to the following:

$$\text{Water Solubility \%} = \frac{W_0 - W_1}{W_0} \times 100$$

where  $W_0$  is the initial weight and  $W_1$  is the residual weight.

**Determination of Residual Sodium Perborate.** Residual SPB is determined according to a reported method.<sup>41</sup> The method is based on determining the amount of available oxygen, total alkali, and sodium oxide content of the oxidized starch (HOS) after repeated washing with 80/20 ethanol/water.

**Determination of available oxygen.** Available oxygen is determined by titration of a solution of the material in dilute sulfuric acid against standard potassium permanganate solution.

Calculation

$$\text{Available Oxygen, Percent by mass} = \frac{0.8 \times V \times N}{M}$$

where  $V$  = volume in mL of 0.01N potassium permanganate solution used in titration,  $N$  = normality of potassium permanganate solution, and  $M$  = mass in g of sample taken for test.

**Determination of total alkali (as  $\text{Na}_2\text{O}$ ) and borate (as  $\text{B}_2\text{O}_3$ ).** Determination of the sodium oxide content took place by treatment of an aqueous solution of the sample with excess hydrochloric acid, followed by back titration with standard sodium hydroxide solution in the presence of methyl red as indicator. Subsequent titration of the boron oxide with standard solution of sodium hydroxide in the presence of sorbitol and phenolphthalein as indicator.

*Total alkali content.*

$$\text{Sodium Oxide Content, Percent by mass} = \frac{V_1 - V_2}{m} \times 7.75$$

where  $V_1$  = volume in mL of the standard sodium hydroxide solution used in the titration of 25 acid solution,  $V_2$  = volume in mL of the standard sodium hydroxide solution used in the titration of the excess hydrochloride, and  $m$  = mass in g of the test specimen.

*Boron oxide content.*

$$\text{Boron Oxide Content, Percent by mass} = \frac{V_3}{m} \times 8.70$$

where  $V_3$  = volume in mL of the standard solution of sodium hydroxide used after addition of sorbitol, and  $m$  = mass in g of the material taken for the test.

**Fourier Transform Infrared Spectra.** FTIR spectra were recorded on a Perkin Elmer Spectrum 1000 FTIR spectrometer under dry air at room temperature for LOS, MOS, and HOS compared with that of NS. The sample (6 mg) was mixed with 200 mg KBr (IR grade) and about 40 mg of the mixture was used to prepare round disk suitable for the measurements. The FTIR spectra were scanned over the wave number range of 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ .

**X-Ray Diffraction of Native and Oxidized Starches.** Powdered NS, LOS, MOS, and HOS were examined using XRD patterns (Empyrean, pixcel<sup>3D</sup>, Amedipixz collaboration, ANALYTICAL, The Netherlands) with Cu-K $\alpha$  radiation ( $\gamma = 0.15406$  nm) in the  $2\theta$  range from 20° to 80°.

**Thermogravimetric Analysis of Native and Oxidized Starches.**

Thermo gravimetric analysis was carried out using 8–10 mg of the samples (NS, LOS, MOS, and HOS) at a heating rate of 10°C/min and a temperature range from 40 to 550°C using SDTQ600 thermal analyzer. The TGA was conducted with the compounds placed in a high-quality nitrogen atmosphere to avoid oxidation.

**Scanning Electronic Microscopy.** The surface morphology of NS, LOS, MOS, and HOS were examined using SEM (JEOL JXA-840) electron probe microanalyzer, Japan. The sample images were recorded with an acceleration voltage of 20 kV. Examination took place by mounting the samples on stub with double stick adhesive tape and coated with gold in a S150A sputter coater unit (Edwards, UK). The gold film thickness was 150 Å.

## RESULTS AND DISCUSSION

### Tentative Mechanism of the Synthesis of Oxidized Starch

SPB,  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ , is considered as a SPB containing hydrogen peroxide. When dissolved in water SPB releases back hydrogen peroxide [eq. (1)].



The oxidation effect is attributed to the perhydroxyl anions ( $\text{HO}_2^-$ ) formed when hydrogen peroxide is present in aqueous solution in dissociation equilibrium with perhydroxyl anions ( $\text{HO}_2^-$ ) [eq. (2)].



The perhydroxyl anions ( $\text{HO}_2^-$ ) may further generate other active species according to [eq. (3)].<sup>42</sup>



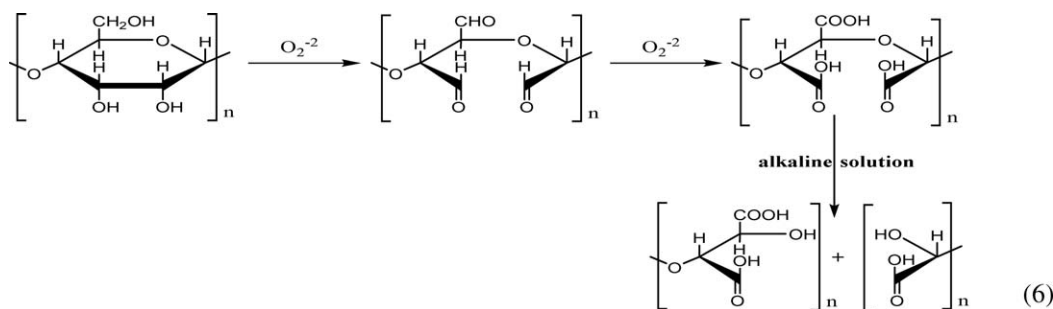
The perhydroxyl radical ( $\text{HO}_2 \cdot$ ) may also dissociate to anion  $\text{O}_2^{-2}$ , known as super oxide, which very recently was considered as an active oxidizing agent [eq. (4)].<sup>43</sup>



There are several popular theories on the identity of active oxygen; it is believed that the reactive species in hydrogen peroxide oxidation is nascent oxygen. This nascent atomic oxygen is claimed to separate easily from perhydroxyl anion [eq. (5)].



Based on the foregoing, starch molecule is oxidized during treatment with SPB by active oxidizing species brought about by decomposition of SPB. As a result, formation of carbonyl groups occurs at C2, C3, and/or C6 and this step is probably rate limited. Once the carbonyl groups are formed, they are rapidly oxidized. Presence of ketonic groups at C2 and C3 help breaking glucosidic bonds<sup>38</sup> and, in turn, the starch chains are simultaneously cleaved via  $\beta$  elimination as shown in eq. (1), which results in reduction of molecular weight of starch.



### Carboxyl and Carbonyl Groups of NS, LOS, MOS, and HOS

The magnitude of carboxyl and carbonyl groups, expressed as meq/100 g starch, signifies the extent of oxidation of NS. The results in Figure 1(a,b) show the carbonyl and carboxyl contents of native and three oxidized maize starches (LOS, MOS, and HOS) at three SPB concentrations (0.25, 0.5, and 1 g of SPB/5 g starch).

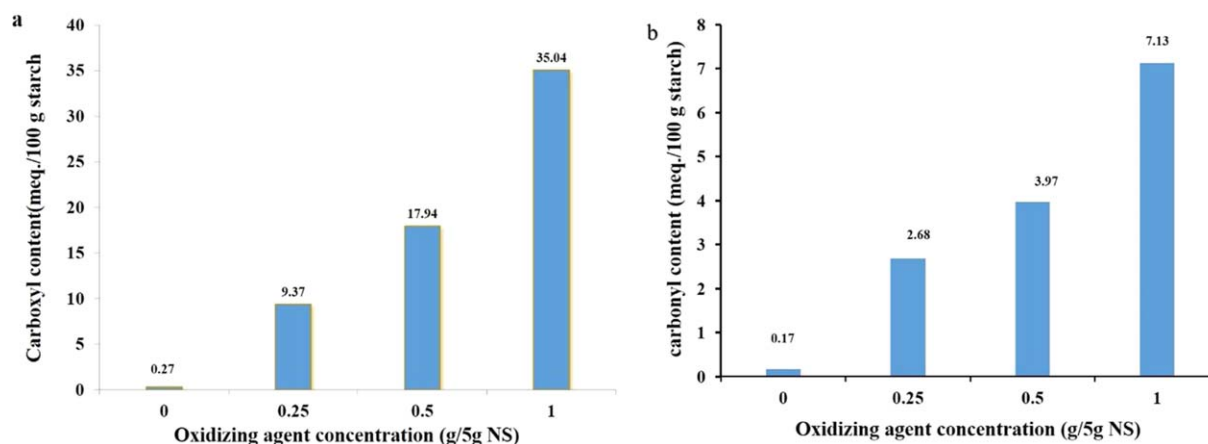
Figure 1(a) shows that incorporation of SPB (0.25 g/5 g NS) to produce LOS increases the carbonyl content from 0.17 for NS to 2.68 meq/100 g starch for LOS. Further increase in the concentration of SPB from (0.25–1 g/5 g starch) to produce MOS and HOS is accompanied by a marked increase in the carbonyl content. This is logical and could be ascribed to abundance of active oxidizing species at higher SPB concentrations. The active species attack the starch molecules at C2 and C3 thereby converting them to carbonyl groups as shown by the scheme of SPB oxidation reactions.

Figure 1(b) shows the carboxyl content of native and oxidized maize starches using different concentrations of SPB. Obviously, results of the carboxyl contents obtained using different SPB concentrations to bring about LOS, MOS, and HOS exhibit a trend which is similar to those of the carbonyl groups. Thus, NS displays the least amount of carboxyl content (0.27 meq/100 g starch). The carboxyl content markedly increases upon oxidation of starch using 0.25 g SPB to reach a value of 9.37 meq/100 g starch. The carboxyl content increases significantly from 9.37 to 17.94 meq/100 g starch when the amount of SPB increases from 0.25 to 0.5 g/5 g starch. The carboxyl content

reaches the highest value of 35.04 meq/100 g starch upon using SPB at a concentration of 1 g/5 g starch. The progressive increment in the carboxyl contents of the oxidized starches by increasing SPB concentration may be attributed to progressive oxidation of the carbonyl and/or hydroxyl groups of starch molecules under the abundance of SPB decomposition products at higher SPB concentrations. It follows from this that oxidation of native maize starch with SPB yields mixed type oxidized starch by virtue of acquiring acidic (carboxyl) and reducing (carbonyl) groups. Stated in other words, the SPB is not a specific oxidizing agent like, for example, the periodate, which gives rise to only reducing type oxidized starch.

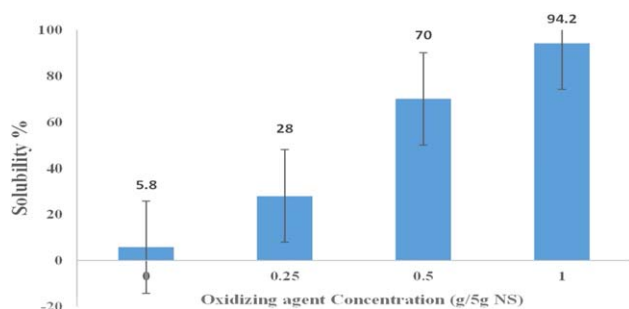
### Effect of Sodium Perborate Concentration on the Solubility of Native and Oxidized Starches

Figure 2 shows the effect of increasing the concentration of SPB on the solubility of oxidized starch as brought about thereof that SPB oxidation of NS causes significant enhancement in the solubility of NS from 5.8 to 94.8% depending on the concentration of SPB in the oxidation medium. The increment in solubility of NS after oxidation comes as a result of depolymerization and structural weakening of the starch granule as well as the formation of the solubilizing carboxyl groups formed under the influence of the oxidation.<sup>44</sup> It is well known that high swelling power will contribute to high solubility. When the granule swells larger, more amylose can be leached out to the soluble phase.<sup>45</sup> Therefore, the amount of SPB (1 g/5 g starch) is sufficient to make starch water soluble.



**Figure 1.** Effect of oxidizing agent concentration on the (a) carbonyl contents of native and oxidized starches as well as (b) carboxyl contents of native and oxidized starches. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





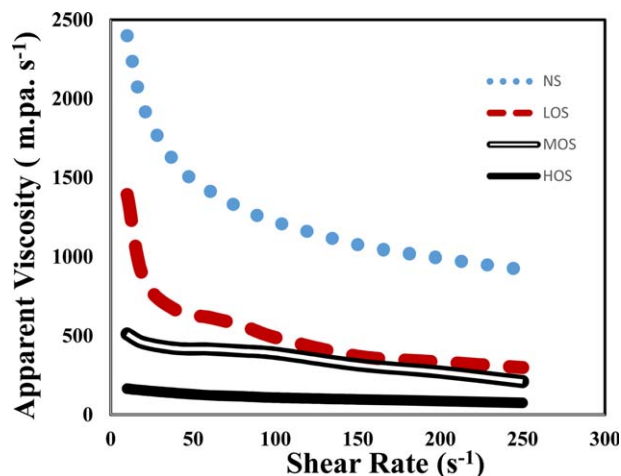
**Figure 2.** Effect of oxidizing agent concentration on the solubility of native and oxidized starches. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Apparent Viscosity of NS and SPB-Oxidized Maize Starches

Figure 3 depicts the apparent viscosity of NS and oxidized starches derived thereof as a function of SPB concentration (at shear rates from 0 to 250  $s^{-1}$ ). The results signify that: (a) regardless of SPB concentration used, increasing the rate of shear is accompanied by decrement in apparent viscosity, (b) increasing the rate of shear to 100 rpm causes dramatic decrement in apparent viscosity followed by marginal decrease at rate of shear of 100–250  $s^{-1}$ ,<sup>46,47</sup> (c) increasing SPB concentration is accompanied by significant decrease in the apparent viscosity, and (d) increasing SPB concentration up to 1 g/5 g starch leads to very low apparent viscosity which levels off even at higher rates of shear.

The viscosity of the three oxidized starches (LOS, MOS, and HOS) significantly decreases by increasing the oxidizing agent concentration, which could be attributed to breaking down the glucosidic linkages as the oxidation proceeds. That is why starch undergoes degradation<sup>44</sup> even when the oxidation is carried out under mild conditions. Decrement in apparent viscosity could be associated with glucosidic bond session particularly during severe oxidation whereby the molecular weight of starch decreases. SPB oxidation of starch brings about ketonic groups at C2 and C3, a situation which eases cleavage of the glucosidic linkages.<sup>48</sup> C1 position is weakened through monomeric ring (i.e., glucose unit) opening and shortening the starch chain molecules. Hence, the extent of starch oxidation depends on the concentration of oxidant (SPB).

The current oxidized starches prepared in this study using SPB as oxidant was compared with commercial oxidized starch prepared using APS as oxidizing agent which applied in the indus-



**Figure 3.** Effect of level of oxidation on the apparent viscosity of native and oxidized starches. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

trial scale in the warp sizing sector during the cooking process at Misr Spinning and Weaving Company, El-Mahalla El-Kubra, Egypt. The commercial oxidized starch symbolized as (St-APS) which was prepared through the project entitled “National Campaign for Textile Development, 2008” financed from Academy of Scientific Research and Technology, Egypt.

Table I summarize the chemical and physical properties of native, oxidized, and commercial oxidized starches symbolized as NS, St-APS, LOS, MOS, and HOS.

It was found from Table I that St-APS have values of carbonyl, carboxyl content, solubility in water, and apparent viscosity within the range between MOS and HOS, which indicate that the utilization of SPB as oxidizing agent for NS is more favorable than using APS due to easier removal during the desizing process. In addition, SPB is more stable than APS during storing for long period. It should be mentioned that APS activity decreases by storing for long period (6 months).

### Residual Sodium Perborate Content

Amount of residual SPB of HOS after repeated washing was determined as available oxygen, total alkali (as  $Na_2O$ ), and borate (as  $B_2O_3$ ) as described in the “Experimental” section. Results of these measurements were as shown in Table II.

It is clear from the results displayed in Table II that the amounts of available oxygen, total alkali as well as borate in the

**Table I.** Summarize the Chemical and Physical Properties of Native, Oxidized, and Commercial Oxidized Starches Symbolized as NS, St-APS, LOS, MOS, and HOS

Oxidized starch	Carboxyl content meq/100 g	Carbonyl Content meq/100 g	Solubility % in water	Apparent viscosity (Pa $s^{-1}$ ) at 250 rate of shear
NS	0.27	0.17	5.8	919
St-APS	21	5.11	76.8	175
LOS	9.37	2.68	28	299
MOS	17.94	3.97	70	210
HOS	35.04	7.13	94.2	75

**Table II.** Summarize the Residual Components of SPB after Repeated Washing in HOS Powder

Analysis of residual components of SPB	Values of residual components of SPB in HOS powder
Available oxygen	0.001%
Sodium oxide (as Na <sub>2</sub> O)	0.155%
Borate (as B <sub>2</sub> O <sub>3</sub> )	0.261%

HOS, which represents the highest concentration of SPB used, are very little. This could be explained in terms of: (1) the consumption of SPB in the oxidation process and (2) the purity of the oxidized starch prepared after the washing process.

#### Fourier Transform Infrared Spectra

The progress of oxidation along with creation of reducing groups could be observed by FTIR spectra. The FTIR spectra of NS, LOS, MOS, and HOS are shown in Figure 4. For NS, the characteristic absorption band occur at 3435.7 cm<sup>-1</sup>, revealing the presence of O—H stretching vibration of OH groups in the glucose units, beside the absorption band at 2926.43, 1450.02, and 1370.11 cm<sup>-1</sup> ascribe to the C—H stretching and bending modes of the methylene groups.<sup>49</sup> The peak at 1640.1 cm<sup>-1</sup> originates from the bending vibration of H—O—H in the absorbed H<sub>2</sub>O. The peaks at 1155, 1080, and 1020 cm<sup>-1</sup> reflect the stretching mode of C—O—C linkages in the glucosidic rings. For the three oxidized maize starches (LOS, MOS, and HOS), it is observed that the creation of new absorption peak of carbonyl groups at 1735.6 cm<sup>-1</sup> can be attributed to the formation of carboxyl and carbonyl groups upon oxidation with SPB oxidant.<sup>14,49</sup> Based on these data, it is logical that acidic and reducing (carboxyl and carbonyl) groups are formed within the starch macromolecules through oxidation using SPB. Meanwhile, the intensity of the O—H stretching vibration absorption of OH groups in the glucose units is strikingly reduced; a point which implies that oxidation occurs at OH groups located at C2, C3, and C6 of the glucose units<sup>14,50</sup> of the molecular chains of starch.<sup>7</sup>

It is as well to report that increasing the degree of oxidation results in enhanced absorption at 1735.6 cm<sup>-1</sup> suggesting greater formation of acidic and/or reducing groups. The results conclude that NS could be oxidized using SPB, and the oxidation is mainly occurring at the starch hydroxyls whereby acidic and reducing groups are formed.<sup>27,50</sup>

#### XRD of NS and the SPB-Oxidized Maize Starches

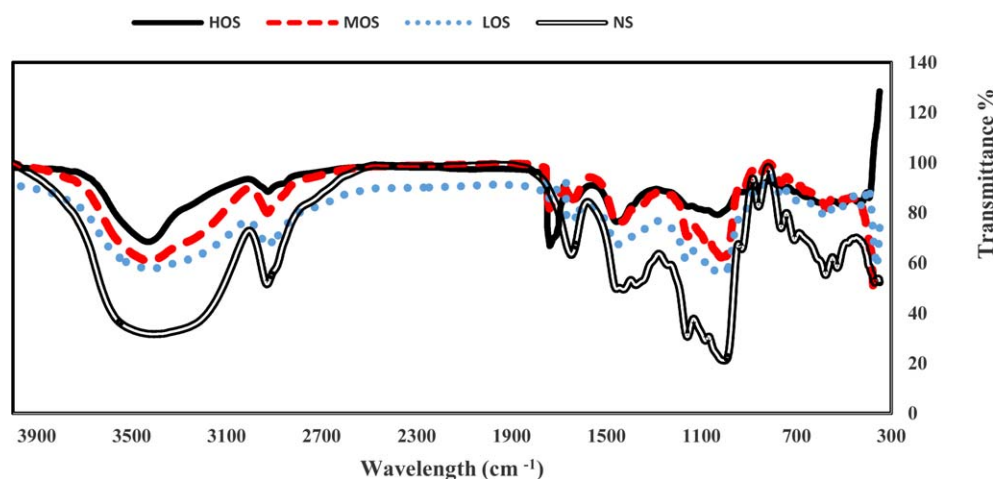
Starch is a semicrystalline polysaccharide existing in nature in the form of granules. The XRD of NS and the three SPB oxidized starches are illustrated in Figure 5. Figure 5 reveal that the NS has sharp peaks at 11.4, 15.3, 17.2, 18.1, and 23.3°, displayed the ideal pattern of type A native maize starch.<sup>51</sup>

When NS is subjected to oxidation with SPB at 90°C, the starch granules collapse forming gelatinized starch. In addition, the SPB molecules penetrate into starch granules and completely destroy the crystalline structure. Figure 5 also shows that the intensity of peaks of NS at 11.4, 15.3, 17.2°, 18.1, and 23.3° disappears in case of the oxidized starches indicating that the crystallinity of starch diminishes along with increasing the concentration of SPB.<sup>52</sup> In addition, the amorphous structure significantly increases by increasing SPB concentration and becomes broad when 1 g SPB/5 g maize starch was used. Moreover, there is no peak in the X-ray diffractogram of starch treated with high concentration of SPB; as is evident, HOS exhibits completely an amorphous phase.

These data confirm the previous results, which speak of: (a) formation of carbonyl and carboxyl groups along with the disruption of starch macromolecules, (b) significant enhancement in solubility upon oxidation, and (c) severe decrement in the apparent viscosity of the oxidized starches under investigation, i.e., LOS, MOS, and HOS.

#### Thermal Gravimetric Analysis

Thermal analysis of NS, LOS, MOS, and HOS using the TGA technique was conducted for determination of temperatures and rates of pyrolysis. To do so, an accurate weight of each of the aforementioned samples was heated from 50°C to 550°C using a heating rate of 10°C per minute in nitrogen atmosphere.



**Figure 4.** FTIR of native and oxidized starches (a) NS, (b) LOS, (c) MOS, and (d) HOS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

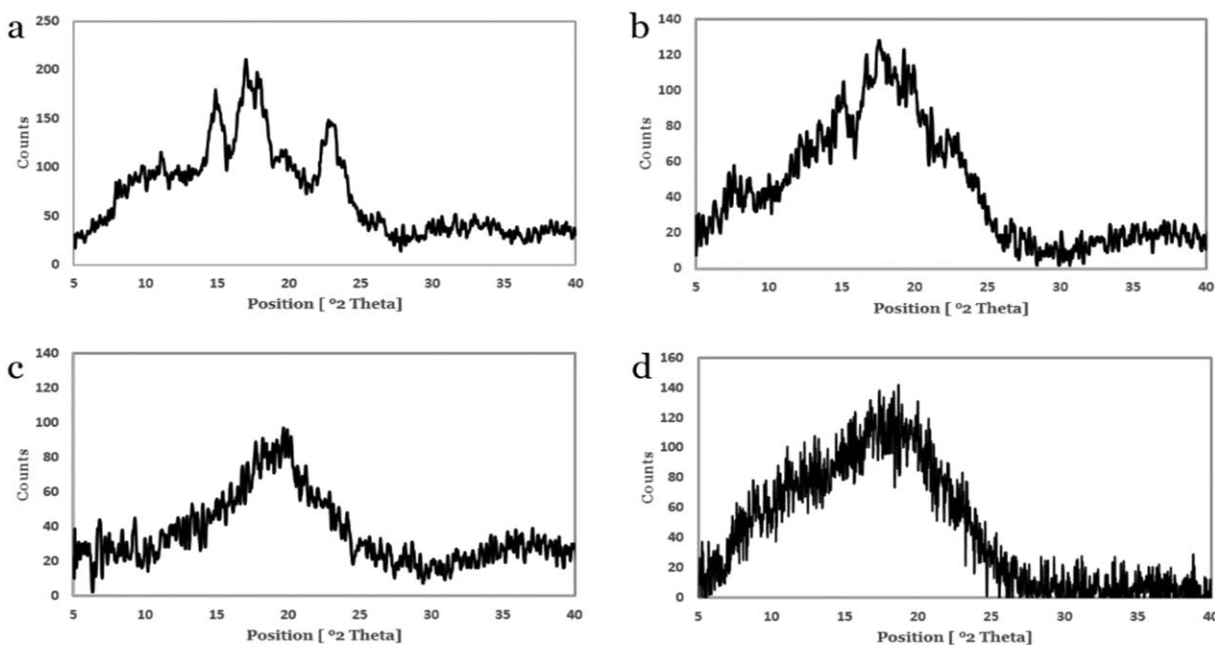


Figure 5. XRD of native and oxidized starches (a) NS, (b) LOS, (c) MOS, and (d) HOS.

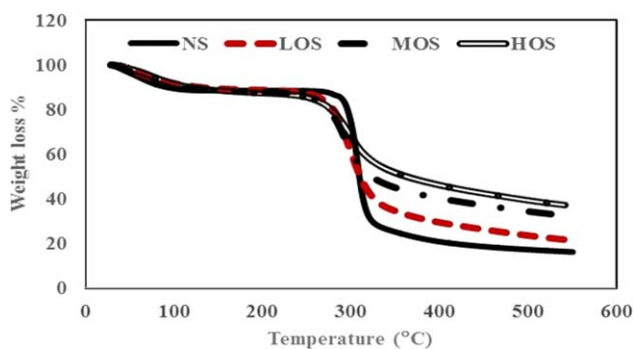


Figure 6. TGA of native starch and oxidized starches. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 shows the TGA curves of NS, LOS, MOS, and HOS, respectively. The figure shows the percentage loss in weight as a function of temperature. Three distinct zones can be seen: (a) an initial weight loss due to volatile materials (largely water) at

around 100°C, (b) main weight loss zone due to the decomposition of starch/or oxidized starch. This zone is characterized by a single state decomposition of NS, LOS, MOS, and HOS, and (c) residual weight due to solid content residue.<sup>53</sup>

Table III discloses the relationship between types of starch and their loss of weight percentage at the temperature of pyrolysis. It is clear that the thermal stability of the samples follows the order: HOS > MOS > LOS > NS.

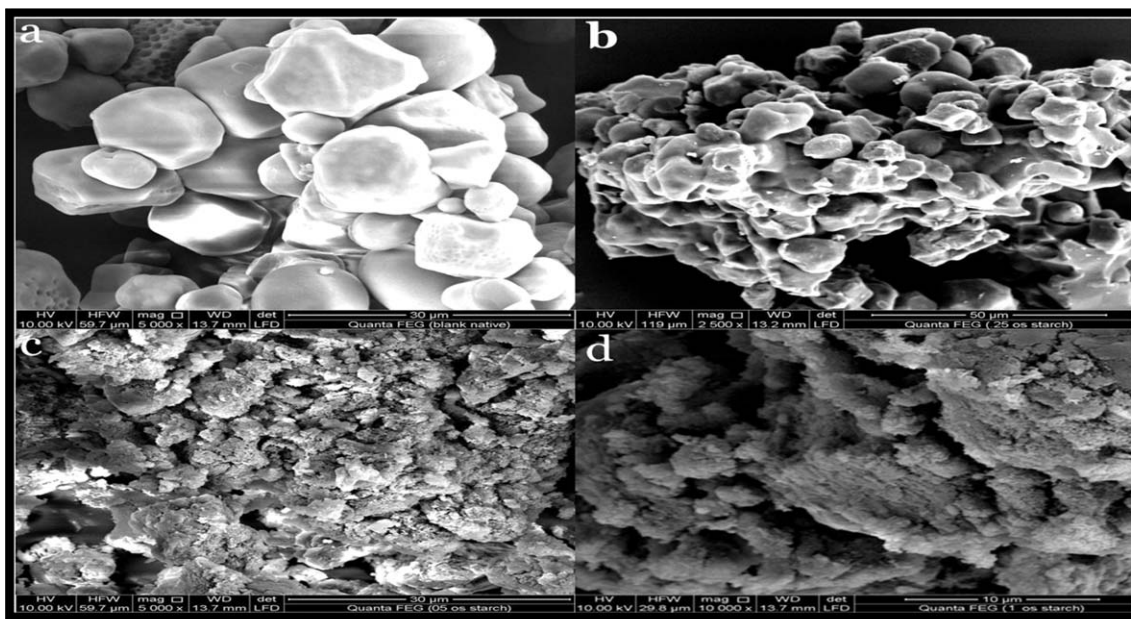
Subjecting NS to oxidation leads to significant changes in its structure via formation of the carbonyl and carboxyl groups with values changes by increasing the extent of oxidation. The residual content (37.11%, 31.99%, 20%, and 16%) for HOS, MOS, LOS, and NS, respectively, reveals that the higher thermal stability of HOS, which may be, ascribed to the abundance of carbonyl, carboxyl content which enriched the thermal stability even at highly elevated temperature.

It is also seen (Table III) that the TGA analysis for LOS, MOS, and HOS are characterized by single stage of decomposition. The

Table III. Main Characteristics of TGA of NS, LOS, MOS, and HOS

Sample	Evaporation		Decomposition temperature		Main decomposition				Residual solid	
	$W_t$	$T$	$T_0$	$T_\infty$	Remaining weight		$W_t$ loss %	Rate/ $T$	$W_t$	$T$
					$W_0$	$W_\infty$				
NS	11.38	87.41	274.34	332.2	87.52	23.57	63.95	1.1	16	550
LOS	10.22	96.73	261.66	321.5	84.99	37.59	47.4	0.79	20	558
MOS	8.91	97.62	262.31	319.8	84.4	36.4	36.4	0.63	31.99	553
HOS	7.06	100.2	258.81	311.2	84.4	27.1	27.16	0.51	37.11	541

$W_t$ , weight loss %;  $T$ , temperature of evaporation phase and residual content;  $T_0$ , initial temperature of decomposition phase;  $T_\infty$ , final temperature of decomposition phase;  $W_0$ , initial weight of decomposition phase;  $W_\infty$ , final weight of decomposition phase.



**Figure 7.** SEM of native and oxidized starches (a) NS, (b) LOS, (c) MOS, and (d) HOS.

appearance of a single stage of decomposition reflects the uniformity of the oxidized maize starches where short chains of the oxidized starches distributed regularly along the starch molecules.

#### Scanning Electronic Microscopy

SEM was used to monitor the morphology of native and oxidized maize starch granules, viz, NS, LOS, MOS, and HOS. Thus, Figure 7(a–d) depicts SEM of native and the oxidized maize starches. Figure 7(a) shows irregular shape for NS and the selected granules have heterogeneous particle size distribution which ranged from 2 to 20  $\mu\text{m}$  in diameter.<sup>7</sup> Due to oxidation reaction [Figure 7(b–d)], the resultant starches acquire rough surfaces and definiteness edges,<sup>54</sup> which could be ascribed to erosion by SPB oxidant. These defects in the resultant oxidized starches morphology increases by increasing the oxidation extent.

#### CONCLUSIONS

Oxidation of native maize starch using SPB at three different concentrations yields three levels of oxidized starches. The latter include low, medium, and highly oxidized starches: nominated as LOS, MOS, and HOS, respectively. The ultrafine structures of these oxidized starches along with NS were monitored using world-class facilities. Results obtained bring into focus conclusions given below:

- The FTIR and XRD patterns indicate the creation of carbonyl groups and a decrease in the crystallinity of starch during oxidation in accordance with the results of carbonyl and carboxyl groups obtained through chemical analysis.
- The oxidized starches display increased solubility and decreased apparent viscosity—vis-a-vis—NS upon increasing the extent of oxidation.
- The resultant oxidized starches have greater uniformity and display greater thermal stability than the native maize starch and follows the order: HOS > MOS > LOS > NS when all these substrates are subjected to thermal gravimetric analysis.

- SEM clarify that the surfaces of the three oxidized starches became rough and the edges lost completely their definiteness upon oxidation.
- The marginal amount of the residual components of SPB after repeated washing in the resultant HOS powder was found.

The above ultramicrostructural features of oxidized starches brought about by treating native maize starch with SPB advocate their use in different applications. Of these, we have indeed used with great success the perborate-oxidized starches in textile warp sizing on industrial scale [Misr company of Spinning and Weaving in El-Mahalla El-Kubra (Egypt)]. Their use in the medical domains is in progress.

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