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OXIDIZED MAIZE STARCH: CHARACTERIZATION AND ITS EFFECT ON THE BIODEGRADABLE FILMS

I. CHARACTERIZATION OF MAIZE STARCH OXIDIZED BY SODIUM HYPOCHLORITE

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ABSTRACT

The effects of hypochlorite level, i.e. 0.5; 1 and 2 active chlorine g/100g starch, on the structure and physicochemical properties of oxidized maize starch were investigated. The obtained results show that oxidation degree grew up with increasing hypochlorite concentration, especially, the carboxyl content saw higher increase than the content of carbonyl. SEM images indicated that surface of oxidized maize starches were rougher than native starch. The surface of oxidized starches became rougher with increasing hypochlorite level in comparison with native starch. However, the DSC results illustrated that there was no significant difference of gelatinization temperature between the native starch and oxidized starches.

Keywords: sodium hypochlorite, maize starch, oxidation, starch oxidized.

1. INTRODUCTION

Starch is a kind of low-costly renewable and biodegradable polymer and has been applied in academic research and industry for the past few decades. However, native starches was limited by their low thermal stability, susceptibility to extreme pH conditions, as well as strong retrogradation rate etc. Chemical modification is a classical way to effectively improve the functionalities of starch and makes it appropriate for various industrial uses. Oxidation as a form of chemical modification, involve the introduction of carboxyl and carbonyl functional groups, by means of subsequent depolymerization of the starch. Oxidized starch is widely used in many industries, particularly in applications where film formation and adhesion properties are desired. Such starches have established to be whiter in color, and have restricted retrogradation [1 - 7].

Oxidized starch is produced by reacting starch with a specific amount of oxidizing agents under controlled temperature and pH [2 - 7]. Hydroxyl groups, primarily at C-2, C-3, and C-6

positions, are transformed to carbonyl and/or carboxyl groups by oxidation [8, 9]. Therefore, the number of these carboxyl and carbonyl groups of oxidized starch indicates the level of oxidation. Several oxidants have been applied to prepare oxidized starch including hydrogen peroxide, air oxygen, ozone, bromine, chromic acid, permanganate, nitrogen dioxide and hypochlorite. The oxidant hypochlorite is the most common method for the production of oxidized starches in an industrial scale [10 – 12].

Starch modified by oxidizing agent presents changes in its molecular structure resulting in a raw material with different characteristics. The concentration of sodium hypochlorite employed for the oxidation of starch depends on the desired degree of modification. Garrido oxidized cassava starches with NaClO at three different concentrations (0.8, 2.0 and 5.0 %). The results showed that oxidized starches also exhibit higher susceptibility to syneresis, as assessed by the release of liquid during freezing and thawing. Apparent viscosity analysis showed a decrease in peak viscosity of the oxidized starches. X-ray diffractograms showed that the oxidation influenced the extent of cassava starch relative crystallinity found to lie between 34.4 % (native) and 39.9 % (2.0 % active chlorine) [10].

The objective of this work was to modify maize starch with relatively cheap sodium hypochlorite (0.5, 1.0 and 2.0 %) and evaluate selected characterization of the modified starches oxidation with desire to extent maize starch applications to a wider range.

2. EXPERIMENTAL

2.1. Material

Native maize starch was obtained from ASEA-VNPICO-FOODS Ltd. Company, Thanh Liet, Thanh Tri, Ha Noi, Vietnam.

Sodium hypochlorite containing approximately 80 % active chlorine (w/w) was obtained from China. Accuracy active chlorine was determined by chemical titration according to method Garrido et al used [10]. The sodium hypochlorite was properly diluted and a quote of 10 mL was transferred to an Erlenmeyer, added of 30 mL of potassium iodide (10 %, w/v) and 30 mL of acetic acid 1:2 (v/v). This solution was titrated with 0.1 M sodium thiosulphate to a light yellow color, when five drops of a 0.5 % (w/v) starch solution were added an the titration followed until the solution became colorless. Active chlorine content was calculated by using the equation:

$$\text{Active chlorine} = (V \times fc \times 0.3722)/(Vs \times d) \times 10 \times 0.953,$$

where: V is 0.1 M thiosulphate solution volume (mL); fc is correction factor of the 0.1 M thiosulphate solution; Vs and d are volume of the sample in mL and density of the sample in g/L, respectively.

All other chemicals used in the study were of analytical grade.

2.2. Preparation of oxidized starch

Hypochlorite-oxidized maize starch was prepared as previously described (Fonseca et al., [12]) with some modifications. A maize starch sample (200 g dry basis (d.b.)) was suspended in 500 mL of distilled water in a glass reactor of 1 L, heated at 40 ^{o}C and subjected to a sodium hypochlorite treatment. The pH of the starch slurry was adjusted to 7.0 with 0.5 mol equi/L NaOH and 0.5 mol equi/L HCl. After addition of 100 ml buffer solution Na_2HPO_4 + NaH_2PO_4 (pH = 7), the sodium hypochlorite was added in the starch slurry. After the reaction (300 min),

the oxidized starch was filtered, washed twice with distilled water and dried at 40 ^{o}C in the vacuum in 16 h. The same procedure was applied for different active chlorine concentrations (0.5, 1.0 and 2 g/100 g starch).

2.3. Carbonyl and carboxyl contents

The carbonyl content was determined according to the titrimetric method adapted by Fonseca et al. [12]. A starch sample (2 g) was added to 100 mL of distilled water in a 500-mL flask. The suspension was gelatinized in a boiling water bath for 20 min, cooled to 40 ^{o}C, and adjusted to a pH value of 3.2 with 0.1 mol equi/L HCl. A hydroxylamine reagent (15 mL) was then added to the mixture. The flask was stoppered and placed in a 40 ^{o}C water bath for 4 h with slow stirring. The excess hydroxylamine was determined by rapidly titrating the reaction mixture to a pH value of 3.2 with standardized 0.1 mol equi/L HCl. A blank determination with only the hydroxylamine reagent was performed in the same manner. The hydroxylamine reagent was prepared by first dissolving 25 g of hydroxylamine hydrochloride in 100 mL of 0.5 mol equi/L NaOH, before the final volume was adjusted to 500 mL with distilled water. The carbonyl content was calculated by equation:

$$CO\ (g/100g) = \frac{(Vb - Vs) \times M \times 0.028 \times 100}{W}$$

where: Vb is the volume of HCl used for the blank (mL), Vs is the volume of HCl required for the sample (mL), M is the molarity of HCl (equi/L) and W is the sample weight (dry basis) (g).

The carboxyl content of the oxidized starch was determined according to the method of Fonseca et al. [12]. Approximately 2 g of a starch sample was mixed with 25 mL of 0.1 mol equi/L HCl, and the slurry was stirred occasionally for 30 min with a magnetic stirrer. The slurry was then vacuum filtered through a 150 mL medium porosity fritted glass funnel and washed with 400 mL of distilled water. The starch cake was then 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 a pH value of 8.3 with standardized 0.01 mol equi/L NaOH. A blank test was performed with unmodified starch. The carboxyl content was calculated by equation:

$$COOH\ (g/100g) = \frac{(Vs - Vb) \times M \times 0.045 \times 100}{W}$$

where: Vs is the volume of NaOH required for the sample (mL),Vb is the volume of NaOH used to test the blank (mL), M is the molarity of NaOH (equi/L) and W is the sample weight (dry basis) (g).

2.4. Viscosity of starch paste

The viscosity of starch paste samples were determined using a Flow Cup (Elcometer 2353 ISO Viscosity Cup No 4, Elcometer, England) according to ASTM D 5125. The viscosity was expressed in seconds (s) flow time. Starch samples were prepared follow method of Fonseca et al. [12], the starch weighed directly and distilled water was added to obtain a starch-water ratio of 1:20 (w:w). Then the sample heated to 95 ^{o}C in 3.5 min, and held at 95 ^{o}C for 2.5 min with

mechanical stirring on whole process. After that, the sample was put in cup and determined the time flow. Measurements were performed three times and average the values were reported.

2.5. Scanning electron microscopy (SEM)

Morphological properties of native maize starch and oxidized maize starch were studied by using Scanning Electronic Microscope S4800 (Japan) at Institute of Materials Science, VAST. Subsequently, all of the samples were coated with gold and examined using a scanning electron microscopy under an acceleration voltage of 15 kV at a magnification of 5000x.

2.6. Thermal analysis

The gelatinization characteristics of starches were determined using a differential scanning calorimeter (DSC) which mean Labsys Evo (France) at Institute of Materials Science, VAST. Starch samples (approximately 2.5 mg, dry basis) were weighed directly in an aluminum pan, and distilled water was added to obtain a starch-water ratio of 1:3 (w:w). The sample pans were then heated in presence of air from 30 to 150 ^{o}C at a rate of 10 ^{o}C/min.

3. RESULTS AND DISCUSSIONS

3.1. Carbonyl and carboxyl contents

Carbonyl, carboxyl contents and oxidation degree of oxidized maize starches at various hypochlorite concentrations were illustrated in Table 1. Oxidation with sodium hypochlorite grew up all of the carbonyl and carboxyl content of maize starches. The carboxyl content saw higher increase than the content of carbonyl. The oxidized maize starch with the highest active chlorine concentration (2 g/100 g) showed a higher carboxyl and carbonyl content as compared to other oxidized maize starches (Table 1). The presence of carbonyl and carboxyl groups in oxidized starches is due to oxidation of the hydroxyl groups of maize starch molecules to carbonyl groups and then the carboxyl groups.

Table 1. Carbonyl and carboxyl contents of the oxidized maize starches.

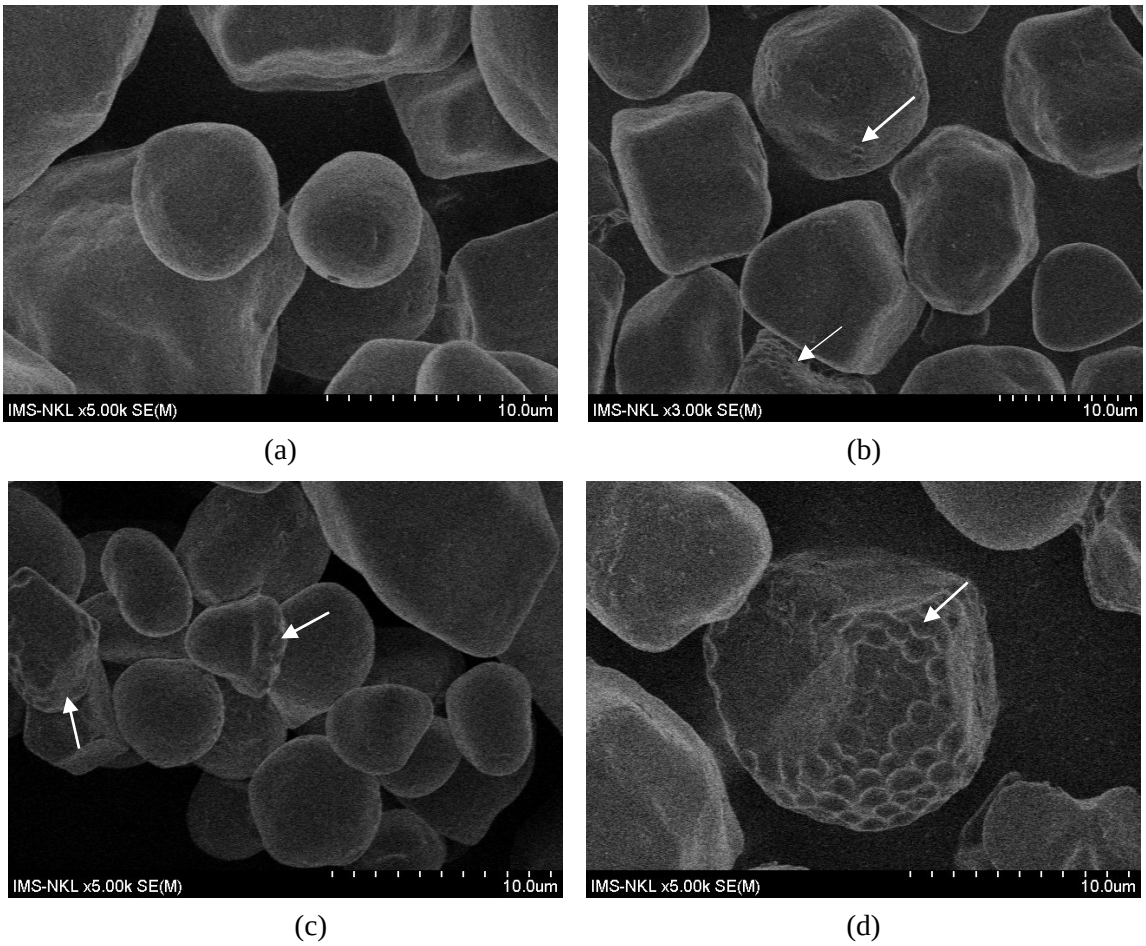
Active chlorine (g/100 g starch)	Carbonyl content (g/100 g)	Carboxyl content (g/100 g)	Sum (CO + COOH)
Native	0.238	-	-
0.5	0.294	0.036	0.33
1	0.336	0.086	0.422
2	0.378	0.194	0.572

Several authors studied the oxidation of cassava and common bean starches with different concentrations of sodium hypochlorite and reported that there was a gradual increase in the carbonyl and carboxyl contents with the increasing concentration of active chlorine [7, 8, 10, 13] while other studied showed the significant differences of carboxyl content with various concentration of active chlorine [12]. Because the level of carbonyl and carboxyl depends on

various factors such as: the source of starch, type and concentration of oxidants, pH, and reaction temperature.

3.2. Starch granules morphology

The scanning electron micrographs of the native and oxidized maize starches are presented in Figure 1.



(a) (b)

(c) (d)

Figure 1. Scanning electron micrographs of maize starch (a) and oxidized starches of 0.5 % (b), 1 % (c) and 2 % (d) active chlorine content.

The SEM data show that native maize starch granules had irregular or truncated shapes. Surface of unmodified maize starch granules was smooth without observable pores. However, for the maize starch modified by 0.5 g chlorine/100 g starch, a slightly roughened surface was observed. Slightly roughened surface due to exo-corrosion was clearly visible after oxidized with higher chlorine active concentration. When studying the effect of the hypochlorite concentration on the physicochemical properties of cassava starch, the results reported that the observed rougher granules and the presence of fissures in oxidized cassava starch [13].

However, there was no changes in the granule morphology of potato starches modified with hypochlorite at ≤ 2 % active chlorine levels [12].

3.3. Viscosity

Viscosity of starch paste expressed via flow time (second) of native starch and oxidation starch are shown on Figure 2.

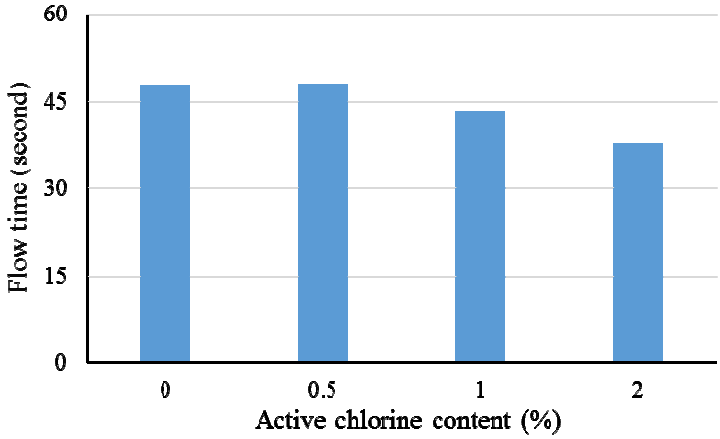


Figure 2. Flow time (second) of native starch and oxidation starch.

Overall, the flow time of starch paste through flow cup reduced when starch was oxidized at higher level of oxidant. There was no different flow time (second) between native starch and starch oxidized by lowest oxidant content, 0.5 % (the flow time of both samples were 48 s). For starch oxidized by oxidant content doubled, leveling off 1 %, the flow time of oxidation starch paste reached 44 s. If the oxidant continuously increased, at 2 %, viscosity of oxidation starch paste reduced to 38 s. Hence, if the oxidant increased, the carboxyl and carbonyl groups content grew up but the viscosity of starch paste reduced. It means that the oxidation process not only transferred hydroxyl group to carbonyl and carboxyl groups but also, more or less, occurred polymer chain scission to create the various molecular compounds with different weights.

3.4. Gelatinization

The gelatinization process is characterized by an endotherm obtained by a differential scanning calorimetry (DSC). The parameters of temperature at the onset of gelatinization (T_o), the temperature at peak (T_p) and the temperature at the end of gelatinization (T_c) are shown in Table 2.

The oxidized maize starches with different concentrations of active chlorine had gelatinization temperatures similar to native starch; however, the oxidized starch with 1 g/100 g active chlorine showed higher gelatinization temperature compared to native starch and to starches oxidized with the other levels of active chlorine (0.5 and 2.0 g/100 g).

The conclusion temperatures (T_c) of the starches oxidized with 0.5 % and 2.0 % active chlorine were insignificantly different from the conclusion temperature of the native starch (Table 2). Many studies have reported the influence of oxidation on the gelatinization properties

of starch, but the results are inconclusive and vary due to starch origin and modification conditions [2, 3, 5, 12].

Table 2. Gelatinization characteristics of the native and hypochlorite-oxidized maize starches.

Active chlorine (g/100 g starch)	Transition temperatures (^oC)*			
	T_o	T_P	T_c	T_c - T_o
Native	71.05	75.30	81.30	10.25
0.5	69.93	74.35	81.23	11.30
1%	72.68	76.24	82.72	10.04
2%	70.29	75.21	81.14	10.85

*Note: * T_o, T_p and T_c are the temperatures at the onset, midpoint and end of gelatinization, respectively.*

Sangseethong et al. [7] found a reduction in the gelatinization temperatures (To, Tp and Tc) of cassava oxidized starches when compared to native starch, they suggested that the negatively charged carboxyl groups introduced during sodium hypochlorite oxidation can readily adsorb water and facilitate hydration, thus weakening starch granules and resulting in gelatinization at lower temperatures. According to Fonseca et all [12], these thermodynamic characteristics of gelatinization can be largely associated with the weakening of the intermolecular bonds responsible for the crystal structure of amylopectin, due to the incorporation of carboxyl groups in the starch granules. In addition, the starch granules undergo a chemical modification that may show, on the surface, disturbances such as fractures and pores, which also facilitate the penetration of water in the granules. Moreover, the oxidation of hypochlorite on maize starch could create particle products with different molecular weights. Variations in the thermal properties of starches from different sources may be due to the granule composition which could be the ratio of amylose/amylopectin, the residual lipids and protein, the molecular structure of amylopectin, morphology and the distribution of starch granules, the products of oxidation process.

4. CONCLUSION

The oxidation with different concentrations of active chlorine affected differently the characteristics of maize starches: (i) The increase in active chlorine concentration increased the intensity of oxidation of the maize starches but reduced the viscosity of starch paste. (ii) With reaction conditions in this article, oxidation attack on starch granules was evident in the form of superficial surface erosion. (iii)There was no significant difference of gelatinization temperatures between the native starch and starches oxidized with different concentration active chlorine.

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TÓM TẮT

TINH BỘT NGÔ OXI HÓA: TÍNH CHẤT VÀ SỰ ẢNH HƯỞNG ĐẾN MÀNG PHÂN HỦY SINH HỌC

I. TÍNH CHẤT CỦA TINH BỘT NGÔ OXI HÓA BẰNG NATRI HYPOCLORIT

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Ảnh hưởng của hàm lượng natri clorit, với tỉ lệ 0,5; 1; 2 gam clo hoạt hóa/100 gam tinh bột đến cấu trúc và tính chất hóa lí của tinh bột ngô oxy hóa đã được nghiên cứu. Kết quả thu được cho thấy, mức độ oxy tinh bột ngô tăng khi tăng hàm lượng natri hypoclorit, đặc biệt, khi tăng hàm lượng chất oxy hóa, hàm lượng nhóm cacboxyl tăng nhanh hơn so với hàm lượng nhóm cacbonyl. Ảnh SEM cho thấy hình thái học bề mặt hạt tinh bột ngô oxy hóa ghồ ghề hơn so với tinh bột ngô ban đầu. Hàm lượng chất oxy hóa tỉ lệ thuận với độ gồ ghề bề mặt của tinh bột ngô oxy hóa. Tuy vậy, kết quả phân tích DSC cho thấy không có sự thay đổi nhiều về nhiệt độ hồ hóa của tinh bột ngô oxy hóa so với tinh bột ban đầu.

Từ khóa: natri hypoclorit, tinh bột ngô, oxy hóa, tinh bột oxy hóa.