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

PART II. INFRARED SPECTROSCOPY AND SOLUBILITY

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ABSTRACT

The oxidization of starch was carried out by reacting starch with a specific amount of hypochlorite, i.e. 0.5; 1 and 2 g active chlorine/100 g starch, under controlled temperature and pH. The effects of hypochlorite level on functional groups and film's solubility of maize starch were investigated. For IR spectrum of oxidized starch, there was a little difference of spectra shape while intensity of some characteristic vibrations showed changes in comparison with native starch IR spectra. To specify, the vibration at 1760 cm^{-1} of oxidized starch corresponding to carbonyl group indicated an increase of intensity while the intensity of absorptions at 3424 cm^{-1} (hydroxyl group) and 1640 cm^{-1} (intra-molecular hydrogen bond) illustrating on oxidized starch IR spectrum experienced a slight decrease in comparison with native starch IR spectrum. The solubility of native starch and oxidized indicated that there was, up to a point, a little scission chain in oxidation process if modifying maize starch by sodium hypochlorite at low concentration ($\leq$ 2 % active chlorine). In addition, the oxidized maize starch film experienced a lower solubility than the film of native starch. It can be explained that the oxidation process, more or less, changed the interaction between amylose molecules as well as the strong intra-molecular bonds due to the appearance of carbonyl, carboxyl and thus reducing the water absorbance of oxidized starch films.

Keywords: sodium hypochlorite, maize starch, oxidized starch, solubility, IR spectroscopy.

1. INTRODUCTION

Starch is a kind of low cost, renewable and biodegradable polymer and has been applied in academic research and industry for the past few decades. However, native starches are 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 make it appropriate for various industrial uses. Oxidation as a form of chemical modification, involves 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, oxygen, ozone, bromine, chromic acid, permanganate, nitrogen dioxide and hypochlorite. The hypochlorite oxidant is the most common approach 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 et al. [10] oxidized cassava starches with NaClO at three different concentrations (0.8, 2.0 and 5.0 %). The results showed that oxidized starches also exhibited higher susceptibility to syneresis, as assessed by the release of liquid during freezing and thawing. Apparent viscosity analysis showed a decrease in viscosity peak of the oxidized starches. X-ray diffractograms indicated that the oxidation process significantly influenced the relative crystallinity of cassava starch oxidized by various NaClO concentrations. The starch relative crystallinity was found to lie between 34.4 % (native) and 39.9 % (2.0 % active chlorine).

The objective of our work is to modify maize starch with relatively cheap sodium hypochlorite (0.5, 1.0 and 2.0 %) and to evaluate selected characterization of the modified starches oxidation with desire to extend maize starch applications to a wider range. In the previous paper, we presented results of effect of sodium hypochlorite on the oxidation degree, starch granules morphology as well as gelatinization characterization [13]. This article would continuously present the infrared spectroscopy, solubility of maize starch oxidized and starch film solubility.

2. MATERIALS AND METHODS

2.1. Materials

The 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 of active chlorine was determined by chemical titration according to the method used by Garrido et al. [10]. The sodium hypochlorite was properly diluted and a quote of 10 mL was transferred to an Erlenmeyer, adding 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, the titration following until the solution became colorless. Active chlorine content was calculated by using the equation: 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 by 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 for 16 h. The same procedure was applied for different active chlorine concentrations (0.5, 1.0 and 2 g/100 g starch).

2.3. Solubility of oxidized starch

The solubility of maize starch was determined as previously described by Fonseca et al. [12] Samples (1 g each) were mixed with 50 mL distilled water in centrifuge tubes. These suspensions were heated at 90 ^{o}C during 30 min. The gelatinized sample was cooled to ambience temperature and then centrifuged at 4500 rpm for 10 min. The supernatant was dried at 110^{o}C until the constant weight was archived, so that the soluble fraction could be quantified. The solubility was expressed as the g/100 g of the dried solid weight based on the dry sample weight. The solubility was calculated by equation:

Solubility = (weight of dissolve solid in supernatant)/(weight of starch sample in dry basis) × 100.

2.4. Fourier transforms infrared (FTIR) spectroscopy

FT-IR spectra of different modified starches were recorded on a Fourier transform infrared spectrometer (Nicole Nexus 670, USA) at Institute for Tropical Technology, VAST, with 4 cm^{-1} of resolution. The transmittance spectra were measured in a range of wavenumber from 4000 to 400 cm^{-1} using KBr pellets which were made from homogenous mixture of KBr powder and fabricated at the same thickness. The starch samples of 1/50 weight ratio were kept at 40 ^{o}C during 48 h in vacuum oven to remove absorbed water before the test.

2.5. Starch film solubility water

Films of maize starches were prepared following the Fonseca method [12]. Starch samples were mixed with distilled water as rate 4.0 and 5.0 g starch/100 mL water. Glycerol was used as a plasticizer with weight ratio of glycerol/starch = 3/10. The film-forming suspension was heated with stirring at 90 ^{o}C during 5 min. After that, the film forming solution was poured on stainless steel and dried at 50 ^{o}C during 48 h in the vacuum oven. Then, the film was stabilized at 25 ^{o}C during 24 h.

The solubility of the starch films was calculated as the g/100 g of solubilized film dry matter after immersion for 24 h in water at 25 ^{o}C. Film discs (diameter of 2 cm) were cut,

weighed, immersed in 50 mL of distilled water. The amount of dry matter in the initial and final samples was determined by drying the samples at 105 ^{o}C for 24 h.

Solubility of starch film = (weight of initial samples – weight of final samples)/(weight of initial samples) × 100.

3. RESULTS AND DISCUSSIONS

3.1. Infrared spectroscopy

The infrared spectroscopy is sensitive to monitor functional groups changes as well as structural changes on starch macromolecules, including helicoidal chain conformation, crystallinity, retrogradation and water content. The infrared spectra of native starches (potato, wheat, regular or waxy corn) present various bands: the band in the region 2900–3000 cm^{-1} correspond to C-H stretching, that in 1160 - 1100 cm^{-1} is relevant to C–O and C–C stretching with some contribution of the C-OH stretching, whereas that in 1077 – 928 cm^{-1} region reflects the asymmetric deformation of C-OH and CH_2 [10,14,15].

IR spectra of native maize starch and maize starch oxidized by sodium hydrochloride at 2 % of active chloride are displayed on Figure 1.

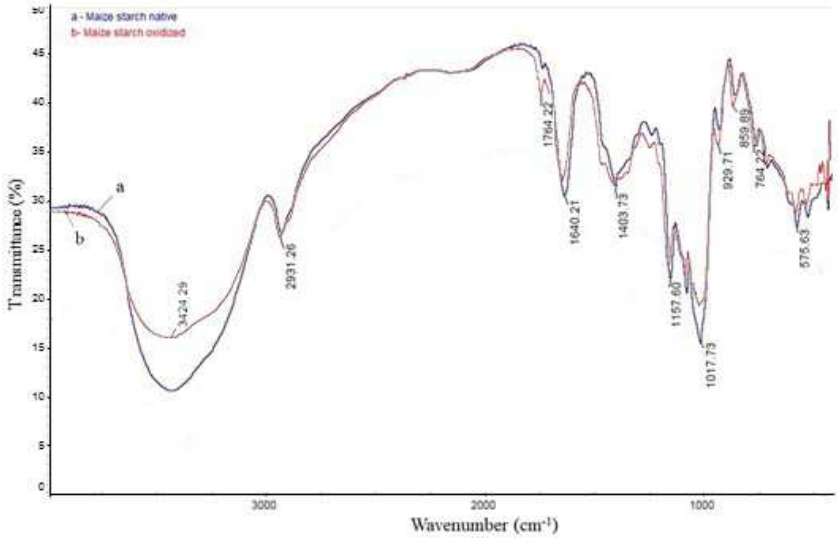

Figure 1. IR spectra of native (a) and maize starch oxidized (b) by sodium hypochlorite at 2/100 of active chlorine/starch weight ratio

As can be seen from Fig. 1, there is a little difference between the graphs of native maize starch (a) and maize starch oxidized by sodium hypochlorite at 2 % active chlorine (b), except for the appearance of stronger absorption intensity at 1760 cm^{-1} corresponding to carbonyl group vibration. The vibration of carbonyl group usually illustrates strong intensity. However, for the maize's IR spectra, the vibration of carbonyl group illustrated a small peak on IR spectrum of maize starch oxidized while this absorption on IR spectrum of native starch was just a tiny peak. It was explained that the carbonyl group content was very low (As the result of chemical titration, total carbonyl contents were of 0.238 and 0.572 g/100 g starch for native and oxidized maize starch, respectively [13]). The IR spectra were suitable with the chemical titration results which investigated that there was a carbonyl creation in the oxidation of maize process.

In addition, absorption at 1640 cm^{-1} (corresponding to the intra-molecular hydrogen bond) and vibration at 3424 cm^{-1} (corresponding to hydroxyl) [13] had a little different shape as well as intensity. In native maize starch, peaks at 3424 and 1640 cm^{-1} were sharper in comparison with those in oxidized maize starch. The optical density of OH and intra-molecular hydrogen bond are presented on Table 1.

Table 1. Optical density of functional group of native starch and oxidized starch.

No	Peak	Native starch	Oxidized starch
1	3424 cm^{-1} (hydroxyl group)	1.49	1.35
2	1640 cm^{-1} (intra-molecular hydrogen bond)	0.43	0.34

It means that the amount of hydroxyl group and intra-molecular hydrogen bond reduced significantly in the oxidized maize starch. In the oxidation of maize starch process by sodium chlorine, hydroxyl group was oxidized to produce carbonyl and carboxyl groups. Consequently, intensity of peak at 3424 cm^{-1} as well as amount of intra-molecular hydrogen bond in starch oxidized reduced. Moreover, for oxidized starch IR spectra, there is an appearance of a shoulder around 3200 cm^{-1} which is assigned to the OH group of COOH and a shoulder around 2900 cm^{-1} supposedly assigned to the C-H group of aldehyde group.

Hence, it is not exaggerating to say that the oxidation process had occurred when modifying maize starch by sodium chlorine. It means that there was a conversion to produce the carbonyl and carboxyl group in the oxidation process.

3.2. Solubility of maize oxidized

Solubility of native and oxidized maize starch are displayed on Figure 2. As can be seen from Figure 2, there is a little difference of solubility between native starch and oxidized starch with low active chlorine ratio (at 0.5 and 1 g/100 g starch), reaching at approximately 8 %. The solubility of oxidized starch at highest active chlorine level (at 2 g/100 g starch) showed the highest degree, levelling off 10.51 %.

According to literature reports, the oxidation of starch has an insignificant effect on the solubility of starch. The study on modifying corn starch by acid and oxidant carried by O.S. Lawala et al. [16] showed that the oxidation did not affect to the solubility of corn starch. There is no difference among the samples. Fonseca et al. [12] illustrated the similar results when they studied the effect of sodium hypochlorite concentration on potato starch oxidation. While some other authors showed that the solubility of oxidized starch illustrated higher solubility increase in comparison with native starch. Liu et al. [14] supposed that the oxidation of starch raised solubility of oxidized starch because of producing hydrophilic functional groups (especially carboxyl). In addition, the chain scission might be occurred in the oxidation process to produce lower molecular weight and thus rising solubility level of oxidized starch.

As can be seen from Fig. 2, there was no substantial change of solubility of native starch and starch oxidized by low active chlorine level (i.e. 0.5 and 1 %). As the chemical titration results [13], the carbonyl contents of native starch and starch oxidized at low active chlorine level, i.e. 0.5 and 1 %, were 0.238; 0.294 and 0.336 g/100 g starch, respectively. In addition, the carboxyl groups were small, levelling off at 0.036 and 0.086 g/100 g starch for starch oxidized by 0.5 and 1 % active chlorine, respectively. It can be seen that although carboxyl and carbonyl groups were produced, it was too small to affect solubility of starch. Moreover, there was a little

difference of viscosity between native and oxidized starches [13]. It means that the oxidation reaction scission, to some extent, occurred insignificantly to produce low molecular weight. Therefore, the solubility of starches was not different between native starch and starches oxidized by low active chlorine degrees.

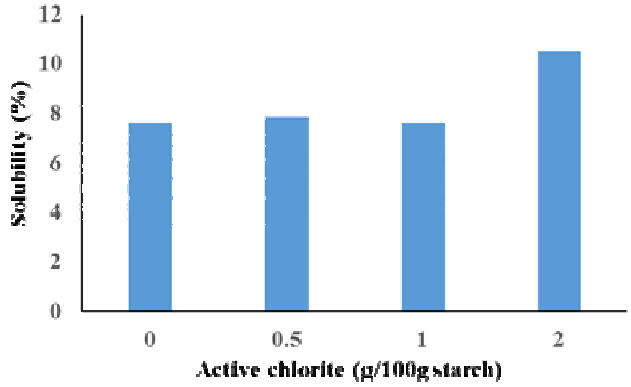

Figure 2. The solubility of native and oxidized maize starch at different active chlorine levels.

Nevertheless, the carbonyl and carboxyl groups' content increased if the content of oxidant rose. Maize starch oxidized by 2 % active chlorine had the highest carboxyl degree, at 0.194 g/100 g starch. The carboxyl content in starch oxidized by 2 % active chlorine was triple that in starch oxidized by 1 % active chlorine. Consequently, the solubility of oxidized starch grew. However, in comparison with solubility of other maize starches oxidized by different active chlorine degrees, solubility of starch oxidized by 2 % active chlorine was higher by a small marginal. The solubility and viscosity of starches exhibited no significant change when increasing active chlorine degree. Hence, it was exaggerating to say that the oxidation reaction of maize starch by sodium hypochlorite at studied concentrations not only transferred hydroxyl group to carbonyl and carboxyl groups, but might also make the polymer chain scission to create various molecular compounds with different weights.

3.3. Maize starch film solubility

The dissolution of a hydrophilic polymer involves penetration or diffusion of water inside and the swelling due to rupture of polymer chains and relaxation. Therefore, the low dissolution rate of the films shows a high cohesion of the matrix.

During 24 h immersion in water, all of maize starch film samples maintained their integrity. The solubility of starch films in water is shown on Table 2.

As can be seen from Table 2, when increasing starch content, the amount of soluble weight of film in water rose. The films prepared from oxidized starch had a lower water solubility compared to native starch. Solubility of maize starch films, which was prepared from maize starch oxidized by 2 % active chlorine, experienced the highest level in the all of samples. Outstandingly, solubility of starch oxidized by 2 % active chlorine showed the highest value while the film based on this starch had the lowest value. It can be explained that the reduction in water solubility of the films of oxidized maize starches can be attributed to the increase of the interactions between the amylose molecules, as well as the strong intra-molecular bonds promoted by the oxidation of the starch, which reduces the capacity of the film to absorb water [12].

Table 2. The solubility of film based on starch oxidized by different active chlorine levels.

No	*Samples based starch*	*Starch weight (g)/100 mL distilled water*	*Solubility (%)*
1	Native starch	4	27.28
		5	28.10.
2	Starch oxidized by 0.5g active chlorine/100 g starch	4	25.27
		5	26.85
3	Starch oxidized by 1g active chlorine/100 g starch	4	19.97
		5	20.63
4	Starch oxidized by 2 g active chlorine/100 g starch	4	19.05
		5	19.78

4. CONCLUSION

The oxidation process is occurred if maize starch reacted with sodium hypochlorite. The difference of structure and functional groups between native starch and oxidized starch were investigated by infrared spectroscopy. The vibration at 1750 cm^{-1} (corresponding to carbonyl group) of oxidized starch spectra has a higher intensity than that of native starch spectroscopy. The oxidation has an insignificant change of solubility of starch if the maize starch is oxidized with content of oxidant leveling off 1 % and lower. If the oxidant content is higher than 1 %, the oxidation has, more or less, scission chain to create the low molecules weight and thus increasing the solubility of starch. However, the carbonyl and carboxyl producing changes the interaction between amylose molecules as well as the strong intra-molecular bonds due to the appearance of carboxyl and thus reducing the water absorbance of starch oxidized films. As results, the oxidized starch film exhibits a lower solubility than native starch.

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REFERENCES

1. Abbas K.A., Sahar K. Khalil, Anis Shobirin Meor Hussin - Modified Starches and Their Usages in Selected Food Products: A Review Study, Journal of Agricultural Science **2** (2010) 90-100.
2. Nathan Levien Vanier, Elessandra da Rosa Zavareze, Vânia Zanella Pinto, Bruna Klein, Fabiana Torma Botelho, Alvaro Renato Guerra Dias, Moacir Cardoso Elias - Physicochemical, crystallinity, pasting and morphological properties of bean starch oxidised by different concentrations of sodium hypochlorite, Food Chemistry **131** (2012) 1255-262.
3. Hui–Tin Chan, Chiu Peng Leh, Rajeev Bhat, Chandra Senan, Peter A. Williams, Alias A. Karim - Molecular structure, rheological and thermal characteristics of ozone-oxidized starch, Food Chemistry **126** (2011) 1019-1024.
4. Yunia Verónica García-Tejeda, Carlos López-González, Juan Pablo Pérez-Orozco, Rodolfo Rendón-Villalobos, Alfredo Jiménez-Pérez, Emmanuel Flores-Huicochea, Javier

Solorza-Feria, C. Andrea Bastida - Physicochemical and mechanical properties of extruded laminates from native and oxidized banana starch during storage- LWT, Food Science and Technology **54** (2013) 447-455.

5. Aisha A.A. Soliman, Nabila A. E1-Shinnawy, Fardous Mobarak - Thermal behaviour of starch and oxidized starch-, Thermochimica Acta **296** (1997) 149-153.
6. Yu-Rong Zhang, Xiu-Li Wang, Guo-Ming Zhao, Yu-Zhong Wang - Influence of oxidized starch on the properties of thermoplastic starch, Carbohydrate Polymers **96** (2013) 358-364
7. Kunruedee Sangseethong, Niti Termvejsayanon, Klanarong Sriroth - Characterization of physicochemical properties of hypochlorite- and peroxide-oxidized cassava starches, Carbohydrate Polymers **82** (2010) 446-453.
8. Ya-Jane Wang, Linfeng Wang - Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite, Carbohydrate Polymers **52** (2003) 207-217
9. Otto B. Wurzburg - Modified starches: properties and uses, CRC Press Inc, 1986.
10. Lúcia Helena Garrido, Egon Schnitzler, Manoela Estefânea Boff Zortéa, Thaís de Souza Rocha, Ivo Mottin Demiate - Physicochemical properties of cassava starch oxidized by sodium hypochlorite, Journal of Food Science and Technology **51** (2014) 2640–2647.
11. Chong W. T., Uthumporn U., Karim A. A., Cheng L. H. - The influence of ultrasound on the degree of oxidation of hypochlorite-oxidized corn starch- LWT, Food Science and Technology **50** (2013) 439-443.
12. Laura Martins Fonseca, Júlia Rosa Gonçalves, Shanise Lisie Mello El Halal, V^ania Zanella Pinto, Alvaro Renato Guerra Dias, Andressa Carolina Jacques, Elessandra da Rosa Zavareze - Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films- LWT, Food Science and Technology **60** (2015) 714-720.
13. Dao Phi Hung, Truong Thi Nam, Mac Van Phuc, Nguyen Anh Hiep, Trinh Van Thanh, Nguyen Thien Vuong - Oxidized maize starch: characterization and its effect on biodegradable films. I. Characterization of maize starch oxidized by sodium hypochlorite - Vietnam Journal of Science and Technology **54** (2016) 347-356.
14. Jianhua Liu, Bin Wang, Long Lin, Jianyou Zhang, Weilin Liu, Jianhua Xie, Yuting Ding - Functional, physicochemical properties and structure of cross-linked oxidized maize starch, Food Hydrocolloids **36** (2014) 45-52.
15. Sacithraa R., MadhanMohan M., Vijayachitra S. - Quantitative Analysis of Tapioca Starch using FT-IR Spectroscopy and Partial Least Squares- International Conference on Innovations In Intelligent Instrumentation, Optimization And Signal Processing "ICIIIOSP-2013", International Journal of Computer Applications, pp. 29-33.
16. Lawala O. S., Adebowaleb K. O., Ogunsanwoa B. M., Barbac L. L., Ilod N. S. - Oxidized and acid thinned starch derivatives of hybrid maize: functional characteristics, wide-angle X-ray diffractometry and thermal properties, International Journal of Biological Macromolecules **35** (2005) 71-79.