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CHARACTERIZATION OF TAPIOCA STARCH OXIDIZED BY SODIUM HYPOCHLORITE

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NGUYEN THANH TUNG[1], NGUYEN VAN KHOI[1], NGUYEN QUANG HUY[1], NGUYEN KIM HUNG[1], THAI HOANG[2]

[1]*Institute of Chemistry - VAST*

[2]*Institute of Tropical Engineering - VAST*

ABSTRACT

The effects of hypochlorite level (NaOCl, 1%, 2% and 4% w/w) on the structures and physicochemical properties of oxidized tapioca starch were investigated. Carboxyl and carbonyl group contents of oxidized starch increased with increasing NaOCl level. Oxidation caused the outer layer of the starch grain surface to erode away and X-ray diffraction patterns of all the starches remained unchanged after oxidation.

I - INTRODUCTION

Oxidized starch has been widely used in various applications such as surface size in textile industry, coating and sealing agent in confectionaries, dough conditioner for bread, binding agent in batter application. Oxidation of starch was performed by reacting starch with many oxidant in which sodium hypochlorite was generally used as oxidizing agent in commercial production. The factors affecting hypochlorite oxidation include pH, temperature, hypochlorite concentration, starch molecular structure and starch origin [1 - 3].

In Vietnam, sodium hypochlorite is a byproduct of soda- chlorine industry. It is an available and cheap reagent. In previous work, the effects of reaction conditions on the hypochlorite oxidation of tapioca starch were studied. Effectiveness of oxidized starch in surface sizing was also tested [4]. In this article, some properties of oxidized tapioca starch were characterized.

II - MATERIALS AND METHODS

1. Materials

Commercial tapioca starch was from Ha Tay Food Company. Sodium hypochlorite was from Viet Tri Chemical Company with active chlorine content 80g/l, HCl, NaOH, $NH_2OH.HCl$ used were of analytical grade.

2. Oxidation [4]

Tapioca starch was suspended in water and the content was stirred with a speed of about 300rpm. The temperature of reaction media was kept constant at 35°C by a water bath. A suitable amount of NaClO solution (active chlorine content 80 g/l) was added to the stirred suspended at reaction temperature. The starch content in the aqueous phase was 700 g/l. The pH of the reaction mixture was maintained at 7.0 during the oxidation course. After the reaction (220 min), the oxidized starch was filtered, washed twice with distilled water and dried at 40°C in the vacuum. The amount of the NaOCl reagent used in the oxidation was

equivalent to 10, 20 and 40g chlorine per kg of starch.

3. Carbonyl and carboxyl contents [4]

- Carbonyl content (%): 4 grams of starch was suspended in 100 ml of distilled water in a 500 ml flask for 20 min, cooled to 40ºC, adjusted to pH 3.2 with 0.1 N HCl and added to 15 ml of hydroxylamine reagent. The flask was stopped and placed in a 40ºC water bath for 4 h with slow stirring. The excess hydroxylamine was determined by titrating rapidly the reaction mixture to pH 3.2 with standardized 0.1 N HCl. A blank determination with only hydroxylamine reagent was prepared by first dissolving 25g hydroxylamine hydrochloride in 100ml of 0.5N NaOH before adjusting the final volume to 500ml with distilled water. Carbonyl content was calculated as follows:

Carbonyl content (g/100g) = [(Blank — Sample) ml x acid normality x 0.028 x 100]/sample weight (g, dry basis)

- Carboxyl content (%): A starch sample (2g) was mixed with 25ml of 0.1 N 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 400ml of distilled water. The starch cake was then carefully transferred into a 500ml beaker, and the volume was adjusted to 300ml 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 450ml with distilled water and titrated to pH 8.3 with standardized 0.01N NaOH. A blank test was performed with unmodified starch. Carboxyl content was calculated as follows:

Milliequivalents of acidity/100g starch = [(Sample — Blank) x molequivalent/l of NaOH x 100]/sample weight (g, dry basis)

Carboxyl content (g/100g) = [milliequivalents of acidity/100g starch] x 0.045.

4. Scanning electron microscopy (SEM)

Morphological properties of unmodified tapioca starch and oxidized tapioca starch were studied by using Scanning Electronic Microscope S4800 (Singapore).

5. X- ray Diffraction

Samples were analyzed between $2\theta = 5^0$ and $2\theta = 50^0$ with a step size $2\theta = 0.002^0$ in a X-ray diffractometer SIEMENS D5000 using a Cu- K_α radiation ($\lambda = 0.15406$ nm), 35 kV and 35 mA.

III - RESULTS AND DISCUSSION

1. Starch yield in oxidation, carbonyl and carboxyl contents

Starch yield, carbonyl and carboxyl contents of oxidized starch at various hypochlorite concentrations were illustrated in table 1.

Table 1: Product yield, carbonyl and carboxyl contents of oxidized starch

	Active chlorine content (g/kg starch)		
	10	20	40
Yield product, %	99.4	97.3	94.2
Carbonyl content, %	0.09	0.13	0.26
Carboxyl content, %	0.37	0.56	1.04

At the lower hypochlorite concentration there were almost no losses at all and at the higher hypochlorite concentration the yield was about 94.2%. The degree of oxidation was characterized by the number of carboxyl and carbonyl groups. At high hypochlorite concentration (40 g/kg), the extent of oxidation was clearly higher than at low oxidant concentration (10 g/kg). At high hypochlorite concentration the amount of carboxyl and

carbonyl groups were 1.04 and 0.26g/100g starch, respectively.

2. Morphological properties

The scanning electron micrographs of the unmodified and oxidized starches at 5.000 and 3.500 x magnifications are presented in Fig. 1.

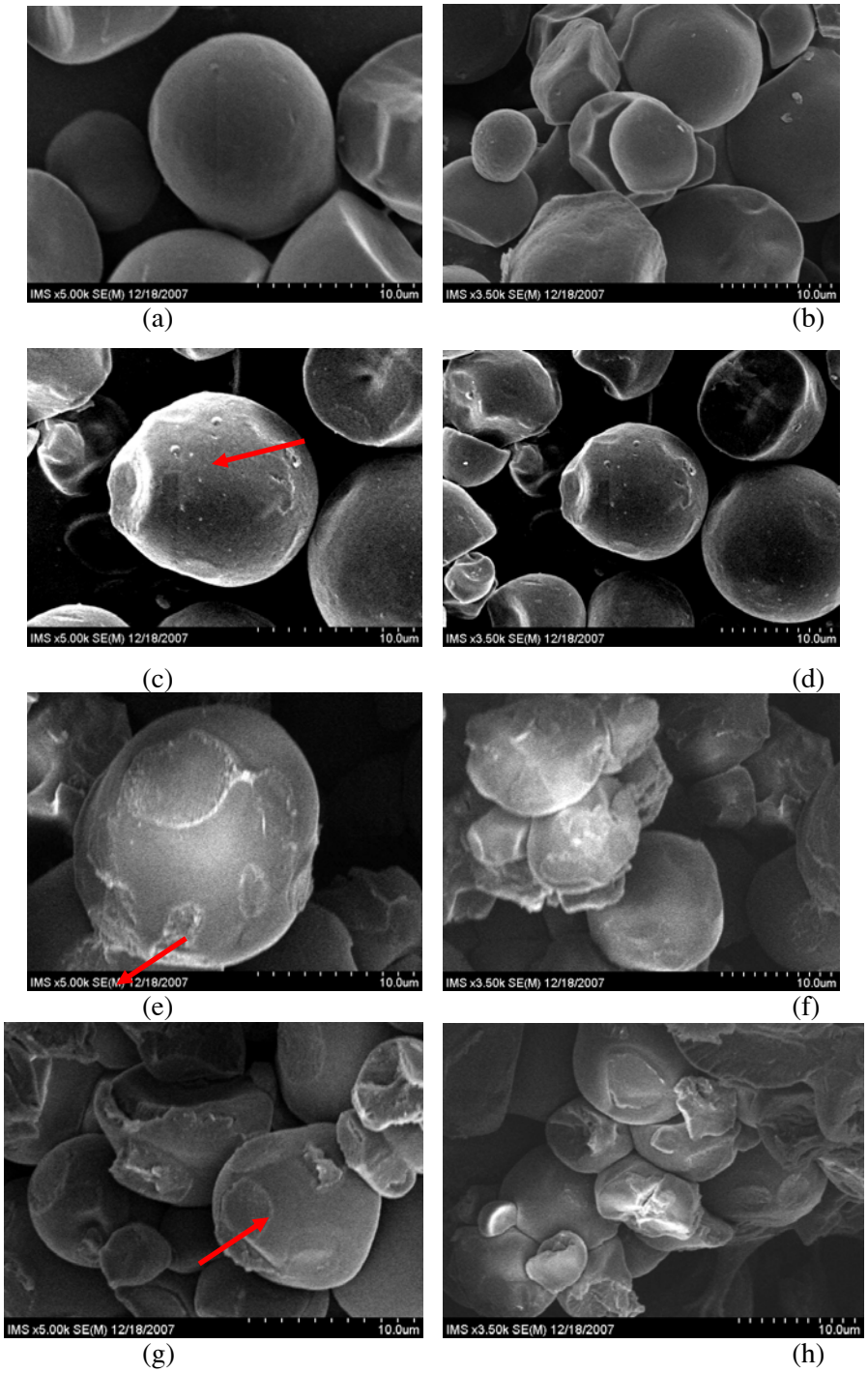

Fig. 1: Scanning electron micrographs (magnification 5000 x and 3.500 x) of tapioca starch (a,b) and oxidized starch of 1% (c, d), 2% (e, f) and 4% (g, h) active chlorine content

Unmodified tapioca starch granules had irregular or truncated shapes with average diameters 12μm. The surface of unmodified starch granules was smooth without observable pores. With 10g chlorine/1kg starch, a slightly roughened surface was observed. A rough surface due to exocorrosion was clearly visible after oxidized with 20 and 40g chlorine/1kg starch. The exocorrosion, which appears all over the starch granules surface as detected by SEM, suggested that amylose was distributed evenly over the entire surface. This would lead to the formation of evenly distributed pores on the surface of the oxidized starch granules.

3. X- ray diffraction

The X-ray diffractograms of unmodified and oxidized starches are depicted in Fig. 2.

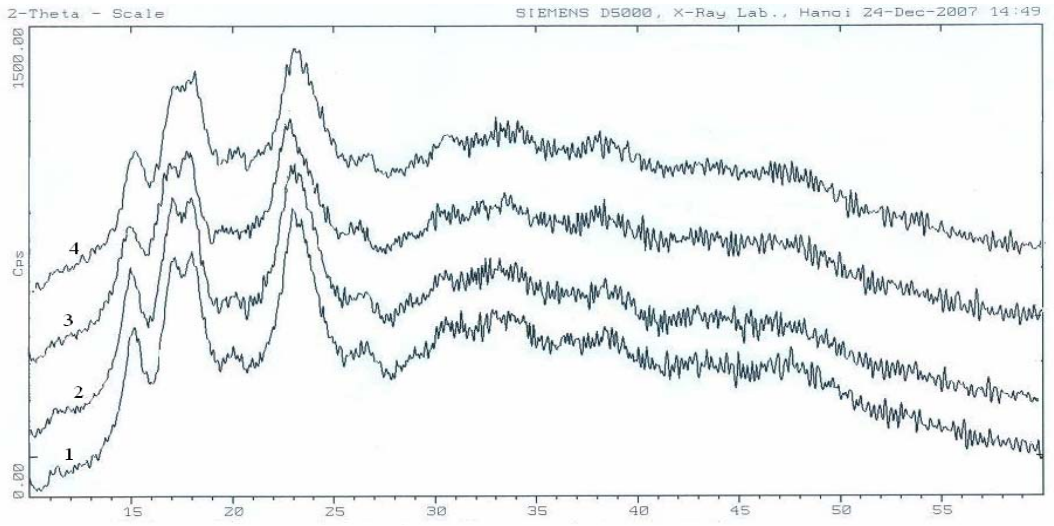

Fig. 2: X- ray diffractograms of unmodified (1) and oxidized starches of 1% (2), 2% (3) and 4% (4) active chlorine content

No significant difference was observed between X-ray pattern of the unmodified and oxidized starches, implying that oxidation took place mainly in the amorphous region.

IV - CONCLUSIONS

Oxidation of tapioca starch with hypochlorite causes the following physico-chemical changes:

- The extent of oxidation increased with higher hypochlorite concentration.

- With reaction conditions in this article, oxidation attack on starch granules was evident in the form of superficial surface erosion.

- Oxidation did not result in any significant changes in the degree of crystallinity of starch because of no change in the upper diffraction peak areas.

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