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EFFECT OF CHEMICAL MODIFICATION ON THE FUNCTIONAL PROPERTIES OF CASSAVA STARCH (*Mannihot esculenta*)

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Abstract

This study assessed and compared the functional properties from modified cassava starches which include ash content, pH, moisture content, gelatinization temperature, swelling temperature, swelling power, swelling volume and solubility with native starch. The modified starches showed great improvement in gelatinization temperature from starch modified with sodium acetate, ammonium phosphate, sodium acetate neutralized with fumaric acid and sodium acetate neutralized with adipic acid having the values of 79°C, 75°C, 71°C, 72°C respectively as compared with 68°C of the native starch; solubility values of 66.7%, 39.1%, 22.4% and 37.06% respectively as compared with 0% of native starch; pH values of 7.54, 7.13, 7.05, 7.01 respectively compared with 5.41 of native starch; moisture content values of 11.45%, 13.05%, 14.35%, 13.50% respectively compared with 10.00% of native starch. However, modified cassava starches showed decrease in ash content with values of 0.03%, 0.12%, 0.18% and 0.04% respectively compared with 0.75% for native starch. Finally, modified starch had a swelling power value of 1.23, 3.76, 3.57, 4.00 compared with a value of 8.40 for native

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starch, and swelling volumes of 1.0, 4.5, 4.2, 5.0 compared with native starch value of 10.5. Therefore, it was noted that the modified starch of *Manihot esculenta* had several improved functional properties which makes it more desirable for specific industrial uses when compared with the native starch of low quality.

INTRODUCTION

Most of the nutritive reserve of many plants is made up of starch. The biosynthesis of starch is a complex process, which could be affected by the growing season. The energy collected by the green leaves is converted to tiny starch granules which is located mostly in the cell interior. Enzymes are responsible for the conversion of sugar to starch (Tester, Karkalas & Qi, 2006).

Starch finds its application in many industrial applications. In pharmaceutical industries, starch could be used to control texture and soft coating and resistant films. Starch may also act as multifunctional component in some food industries, production of adhesives, paper making, etc. (Miyazaki, Hung, Maeda & Morita, 2006).

The modification of starch can be classified into four groups: physical, chemical, enzymic and biological. This paper addressed the chemical method of modification. The chemical method of modification involves the treatment of native starch using different chemical reagents. This may include acetylated, hydroxypropylated or cross-linked starches (Kaur & Singh, 2004).

Chemical method of native starch modification increases the amylopectin component and has the advantage of making it more stable for production of paper, glues, cosmetics, etc. (Hirsch & Kokini, 2002). Chemically modified starch is also more resistant to heat, acid and shearing than native starch. Cross-linked starch is also finds application in surgical dusting powder, canned food and biopolymer packaging bags, etc. (Shildneck & Smith, 2009).

The purpose of this research was to analyze the effect of chemical modification on the functional properties of native starch, which is a valuable and cheap source of carbohydrate in developing countries such as Nigeria.

MATERIALS AND METHOD

The cassava tubers were cultivated and harvested from Unwana Community, Ebonyi State, Nigeria. The chemical reagents used for the chemical modification of the native starch were of analytical grade.

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Preparation of Starch Samples

Cassava starch samples were produced using the modified method of Morthy et al (2006). The cassava tubers were peeled and meshed in a grating machine. The resultant mesh was further ground and water was added in the ratio of 1:4. Filtration of the mesh was carried out using a nylon bag to obtain starch solution. Separation of the starch from water was carried out by sedimentation and decantation processes. The starch was placed in the sun to dry. The sun-dried starch was ground using a pestle and mortar. Then the prepared starch was ready for modification.

Production of Modified Starch using Sodium Acetate

A weight of 150 g of native cassava starch was weighed into a plastic container and 0.2 g of SiO_2 (fluxing agent) was added and mixed for 5min., 20 g of NaOH (alkaline catalyst) was added and mixed for 15 min., 30 g of sodium acetate (cross linking agent) was added and mixed for 10 min. and heat-stirred in a water bath at a constant temperature of 70°C. The mixture was stirred for 30 min. and allowed to cool.

Preparation of Modified Starch using Fumaric Acid and Sodium Acetate

A weight of 150 g of native starch was weighed into a plastic container, 0.2 g of SiO2 was added and stirred for 10 min., 20 g of NaOH (alkaline catalyst) was added and mixed for 15 min. and an amount of 15 g of sodium acetate and 15 g of fumaric acid was added and mixed for 10 min. and heat-stirred in a water bath at a constant temperature of 70°C. The mixture was stirred for 30 min. and allowed to cool.

Preparation of Modified Starch using Adipic Acid and Sodium Acetate

A weight of 150 g of native cassava starch was placed in a plastic container, 0.2 g of SiO_2 was added and mixed for 5min., 15 g of NaOH (alkaline catalyst) and 15 g of adipic acid added and mixed for 10 min. and heat-stirred in a water bath at a constant temperature of 70°C. The mixture was mixed for 30 min. and allowed to cool.

Preparation of Modified Cassava Starch using Ammonium Phosphate

A weight of 150 g of native cassava starch was measured into a plastic container and 2.5 ml of aqueous solution of NaOH was mixed with 5g of ammonium

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phosphate (cross linking agent) to the starch; it was dried in an oven and placed in an air tight plastic container for analysis.

CHEMICAL ANALYSIS

Determination of ash content

An amount of 5 g of starch sample was weighed into a crucible and allowed to form ash. The ash content was calculated using the equation:

$$\% \text{ Ash in sample} = \frac{W_2 - W_1}{\text{Weight of sample}} \times 100$$

Where W_1 is the weight of crucible + sample after ashing. While W_2 is the weight of crucible + sample before ashing.

Determination of pH

This was done using a pH meter (model HG 7310). An amount of 1.5 g of starch dissolved in a glass beaker with 10 ml of water and mixed thoroughly. The pH meter was put in the solution and the value was read.

Determination of Gelatinization Temperature

A weight of 1.5 g of starch sample was dissolved in a glass beaker and 10 ml of water was added. The mixture was mixed and put in a water bath and mixed continually until it thickened and became milky. This is called the gel point and the temperature at this point was taken which is the gelatinization temperature.

Determination of Moisture Content

The moisture content in samples was calculated using the formula

$$\% \text{ Moisture} = \frac{W_2 - W_1}{\text{Weight of sample before drying}} \times 100$$

Where, W_1 is the weight of moisture in sample after cooling. While W_2 is the weight of metal dish + sample

Determination of Swelling Power/Volume and Solubility

The determination of the swelling power/volume was carried out using the method of Hirsch et al (2002). The functional parameters were determined using the following equations:

$$\text{Swelling power} = \frac{\text{Weight of swollen sediment}}{\text{Weight of dry starch}}$$

$$\text{Solubility} = \frac{\text{Weight of dry supernatant}}{\text{Weight of starch sample}} \times 100$$

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RESULT AND DISCUSSION

The starch samples: native starch modified with sodium acetate, ammonium phosphate, sodium acetate neutralized with fumaric acid and sodium acetate neutralized with adipic acid are labeled 1 to 5 respectively as shown in the table below.

Table 1. Analysis of functional properties of starch samples

sample	%Ash	pH	Gel temp (°C)	%Moisture	Swelling Vol. (ml)	Swelling power	Solubility (%)
1	0.75	5.41	68.00	10.00	10.50	8.40	0.00
2	0.03	7.45	79.00	11.45	1.00	1.23	66.70
3	0.12	7.13	75.00	13.05	4.50	3.76	39.10
4	0.18	7.05	74.00	14.35	4.20	3.57	22.40
5	0.29	7.01	72.00	13.50	5.00	4.00	37.06

Ash Content

The ash content of a sample is the non-volatile inorganic matter of a substance which is left after subjecting it to a high temperature. The ash content could be described as an indication of a cleaning process. This trend is obtained from the results of the ash content of the modified starches shown in the table showing that modification process using cross-linking process produces cleaner starches.

pH

The pH of the native starch increased as a result of the modification. It is favourable that the pH of the starch tends toward neutrality so the it be used in industries where a change in the pH of products is not needed.

Moisture Content

The permissible allowable limit for moisture in starch flour 14% (Austin, 2004). Higher moisture values encourage growth of organisms which produces foul odour and off-colour. The table indicated modification using cross-linking increased the moisture content of the modified starches compared with native starch but did pass the maximum permissible limit for moisture in starch (Mahmut & Sosulski, 2000)

Gelatinization Temperature

The purpose of cross-linking treatment is to add inter-molecular bonds at random locations in the starch granule that stabilize and strengthen the granule (Zhao & Whistler, 2004). This trend is seen in the table for all the modified starches. Similar

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thermal properties for cross-linked wheat starch were also reported by Choi and Herr (2004).

Swelling Power, Swelling Volume and Solubility Samples

Depending on the cross-linking agent used it has been reported that the cross-linking process decreases the swelling power, swelling volume and solubility of starches from various sources (Hoover and Sosulski, 2006). All the modified starches indicated a decrease in their swelling power and swelling volume compared with the native starch as shown in the table. The starch modified with fumaric acid has the lowest solubility with 22.4% among the modified starches.

CONCLUSION

The functional properties of the native starch were carried analyzed using different reagents (modification process). The modified starches indicated improved functional properties which makes them suitable for various uses compared with the native starch.

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