

Modification of Cassava Starch for Industrial Uses

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ABSTRACT

Cassava starch modification by cross-linking using four different reagents (ammonium phosphate, sodium acetate, sodium acetate with adipic acid, sodium acetate with fumaric acid) was performed. Functional properties (ash content, pH, moisture content, gelatinization temperature, swelling power, swelling volume, solubility and viscosity) of the modified starch were compared with those of the native cassava starch. The modified starches had varying degrees of improvements in properties in descending order as: modification with sodium acetate, ammonium phosphate, sodium acetate with adipic acid, sodium acetate with fumaric acid. Starch modified with sodium acetate and ammonium phosphate showed great improvement in their gelatinization temperature with values of 79°F and 75°F compared with 69°F of the native starch, solubility of 66.7% and 37.1% compared with 0% of the native cassava starch and had lower and stable viscosities.

Keywords: *Cassava starch, modification, cross linking, functional properties*

1. INTRODUCTION

Starch is one of the most important but flexible food ingredients possessing value added attributes for innumerable industrial applications. The most common sources of food starch are corn, potato, wheat, cassava/tapioca and rice. Cassava is second only to sweet potato as the most important starchy root crop of the tropics (Grace, 1977). It is now grown widely as food crop and for industrial purposes. In Nigeria, cassava is a staple food for both rural and urban areas and in recent years it has been transformed from being a subsistent crop to an industrial cash crop. Starch's use now extends far beyond its original design as a source of biological energy. Practically every industry in existence uses starch or its derivatives in one form or another. In foods and pharmaceuticals starch is used to influence or control such characteristics as texture, moisture, consistency and shelf stability. It can be used to bind or to disintegrate; to expand or to densify; to clarify or to opacify; to attract moisture or to inhibit moisture; to produce smooth texture or pulpy texture, soft coatings or crisp coatings. It can be used to stabilize emulsions or to form oil resistant films. Starch truly serves as a multifunctional ingredient in the food industry. (Miyazaki *et al.* 2006).

Native starches irrespective of their source are undesirable for many industrial applications because of their inability to withstand processing conditions such as extreme temperature (has low thermal resistance), diverse pH and high shear rate (has low shear resistance) (Singh *et al.* 2007), high ability to retrograde, loss of viscosity, syneresis tendency and thickening power upon cooking

and storage particular at low pH. Native starches also yield pastes of poor stability which decreases its shelf life (storage stability) causes shrinkage and the release of water. In order to improve on the desirable functional properties and overcome its limitations, native starches are often modified. Modification, (alteration of the physical and chemical characteristics to improve structural properties) can be used to improve inherent poor physio-chemical properties of native starch thus tailor it to specific industrial applications (Cock, 1982; Miyazaki *et al.*, 2006).

Starch modification can be broadly grouped into four classes namely: physical, chemical, enzymic and biological modifications. Among these modification methods, chemical means is the most frequently used process (Daramola and Osanyinlusi, 2006). Chemical modification of starch involves the treatment of native starch with specific chemicals reagent. This definition includes acetylated, oxidized, lintnerized, pyrodextrinized, hydroxypropylated and cross-linked starches (Kaur *et al.*, 2004).

Modification using the method of cross linking increases the amylopectin content of native starch and makes the starch more stable and particularly useful in adhesive manufacture, paper making and used in frozen foods (Hirsch and Kokini 2002). Cross-linking and substitution are two methods for making modified starches. Cross-linked starch is more resistant to acid, heat and shearing than is native starch (Mirmoghtadaei, *et al.*, 2009). Therefore cross-linked starch is suitable for canned food, surgical dusting powder and other applications (Miyazaki *et al.*, 2006)

In recent years, substantial progresses have been made in obtaining starches from non-conventional botanical sources and studying their functional and physicochemical properties (Zhao and Whistler, 1994; Perez *et al.*, 1997; Hoover, 2001; Nunez-Santiago *et al.*, 2004).

The objective of this study is to evaluate the effect of modification by cross linking on some physicochemical and rheological properties of starch obtained from a species of Nigerian cassava (native starch). Starch extracted from cassava is modified by the method of cross-linking using ammonium phosphate, sodium acetate, sodium acetate with adipic and fumaric acids respectively and its properties (gelatinization temperature, moisture content, pH, viscosity, solubility, swelling power and volume and ash content) determined and compared with that of the unmodified native starch. These results may be useful in finding new applications for this type of cross-linked starch in food and non-food productions.

2. MATERIALS AND METHODS

Freshly harvested cassava tubers (seventeen months old) of specie TMS 55124 were obtained from the student's demonstration farm of the Rivers State University of Science and Technology, Port Harcourt, Nigeria.

2.1 Cassava Starch Preparation

Cassava starch was prepared following the method of Moorthy *et al.*, (1999). Cassava roots were peeled, washed and disintegrated in a grating machine. The resulting cassava mesh was reground and mixed with water in the ratio 1:5 (w/v %). The mesh was filtered through double layer of nylon cloth to obtain starch solution. The starch was separated from the water by sedimentation and decantation. The starch was set in an oven to dry. The native starch was labelled 1.

2.2 Preparation of Modified Cassava Starches

Four types of cross-linked cassava starches were produced as shown in Figure 1 using four different reagents: ammonium phosphate, sodium acetate, sodium acetate neutralized with adipic acid and sodium acetate neutralized with fumaric acid. The modified starches were labelled 2, 3, 4 and 5 respectively.

2.3 Preparation of Modified Starch with Ammonium Phosphate

Weigh 200g of native cassava starch into a plastic container, add 2.4ml aqueous solution of sodium

hydroxide mix thoroughly, add 6g of ammonium phosphate (cross linking agent) to the starch and mix thoroughly, dry in an oven and store in a plastic air tight container at room temperature.

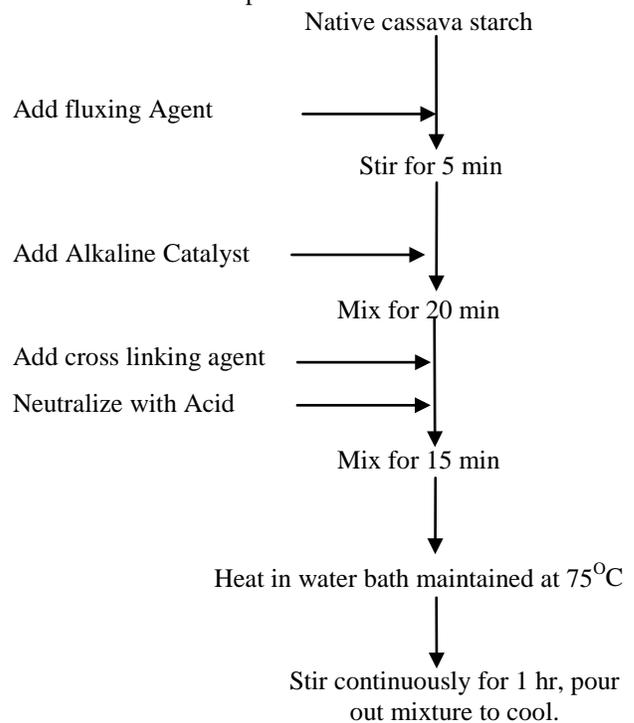


Figure 1: Flow chart for the preparation of modified cassava starch

2.4 Preparation of Modified Starch With Sodium Acetate

Weigh 200g of native cassava starch into a plastic container, add 0.2g of silicon oxide (fluxing agent) to the starch, mix for 5 minutes, add 20g of sodium hydroxide (alkaline catalyst), mix for 20 minutes, add 29g of sodium acetate (cross linking agent) mix for 15 minutes, heat mixture in a water bath maintained at a temperature of 75°C, stir mixture continuously for 1hour, pour out the mixture to cool.

2.5 Preparation of Modified Starch with Sodium Acetate and Fumaric Acid

Weigh 200g of native cassava starch into a plastic container, add 0.2g of silicon oxide, mix for 5 minutes, add 20g of sodium hydroxide (alkaline catalyst), mix for 20 minutes, add 29g of sodium acetate and 14.5g of fumaric acid, mix for 15 minutes, heat mixture in a water bath maintained at a temperature of 75°C, stir mixture continuously for 1hour, pour out the mixture to cool.

2.6 Preparation of Modified Starch with Sodium Acetate and Adipic Acid

Weigh 200g of native cassava starch into a plastic container, add 0.2g of silicon oxide, mix for 5 minutes, add 20g of sodium hydroxide (alkaline catalyst), mix for 20 minutes, add 29g of sodium acetate and 14.5g of adipic acid, mix for 15 minutes, heat mixture in a water bath maintained at a temperature of 75°C, stir mixture continuously for 1hour, pour out the mixture to cool.

3. CHEMICAL ANALYSIS

After extraction and modification of the native starch, some chemical tests were performed to determine thermal and rheological properties of the starches and confirm any improvements in quality of the modified starch when compared with those of the native starches; hence ascertain the impact of modification. All results were the average of duplicate analysis. The ash content, pH, gelatinization temperature, and moisture content were determined according to the methods of Association of Official Analytical Chemists (AOAC, 1984)

3.1 Determination of Ash Content

1.5g of sample was weighed into a crucible of known weight. The crucible was put into a furnace and the sample left to ash. After ashing, the crucible was brought out of the furnace, cooled to room temperature and weighed. The ash content of the sample was calculated using the formula:

$$\% \text{ ash in sample} = \frac{\text{Weight of ash in sample}}{\text{Weight of sample}} \times 100 \quad (1)$$

3.2 Determination of pH

This was determined using a pH meter (model HI 8424 with pH buffer 7). 1.5g of starch sample was dissolved in beaker with 10ml of distilled water and stirred properly. The pH meter was inserted into the solution and the reading taken.

3.3 Determination of Gelatinization Temperature

1.5g of starch sample was dissolved in a beaker with 10ml of distilled water, mixture is stirred, a thermometer inserted and beaker placed in a water bath. The solution was stirred continuously until its colour became milky and thickened. This is the gel point and the temperature at this point was read off as the gelatinization temperature.

3.4 Determination of Moisture Content

Five clean metal dishes were dried in an oven for 15 minutes at 105°C, allowed to cool in a dessicator for 10

minutes and weighed. 2g of each starch sample was put into the dishes, weighed and labelled. The dishes were put in an oven maintained at 105°C for 4 hours; the dishes were removed, placed in the dessicator and allowed to cool for 15 minutes. The dishes were removed and weighed as quickly as possible. The moisture content in the samples was calculated as follows:

$$\% \text{ Moisture} = \frac{\text{Weight moisture in sample}}{\text{Weight of sample before drying}} \times 100 \quad (2)$$

3.5 Determination of Swelling Volume, Swelling Power and Solubility

The swelling power and solubility were determined in accordance with the methods described by Hirsch and KoKini, (2002). The samples were poured into graduated centrifuge tubes appropriately labelled. The solution was stirred, placed in a water bath heated to 95°C while shaking the sample gently to ensure that the starch granules remain in suspension until gelatinization occurs. The gelatinized samples were held at 95°C in the water bath for 1 hour. The samples were cooled to room temperature under running water and centrifuged for 30 minutes at 1000rpm. After centrifuging, the swelling volume was obtained directly by reading the volume of swollen sediment in the tube. The supernatant was separated from the sediment, put in a metal dish, weighed, dried at 105°C for 1 hour, weighed and dried again. The starch swelling power and solubility were determined according to equations (3) and (4).

$$\text{Swelling power} = \frac{\text{Weight of swollen sediment}}{\text{Weight of dry starch}} \quad (3)$$

$$\text{Solubility} = \frac{\text{Weight of dry supernatant}}{\text{Weight of starch sample}} \times 100 \quad (4)$$

3.6 Determination of Viscosity

The Viscosity profile of the native and modified starches was obtained using a viscometer (LvDv I+, Brookfield, USA) following the technique proposed by AOAC, 1884. The gelatinized starch was heated to a desired temperature and placed under the viscometer with the spindle immersed in the beaker. The spindle was set at speeds rate of 10, 20, 50, 100rpm and the viscometer readings taken at these speeds. This procedure is repeated for the all starch samples at temperatures 10°C, 20°C, 30°C, 60°C and 80°C.

4. RESULTS AND DISCUSSION

The results of the various analyses to determine the thermal and rheological properties of the native and modified starches such as the ash content, pH, gelatinization temperature, moisture content, swelling

volume, swelling power and solubility are presented in

Table 1.

Table 1: Result of Quality Analysis of Starch Samples

Sample	% Ash	pH	Gel. Temp. (°C)	% Moisture	Swelling Volume	Swelling Power	Solubility (%)
1	0.153	5.41	69	12.50%	10.5	7.40	0
2	0.133	7.05	75	15.00%	4.5	3.76	37.06
3	0.123	7.54	79	11.75%	1.0	1.23	66.67
4	0.207	5.66	74	14.55%	4.5	3.57	39.40
5	0.033	7.13	77	13.50%	5.0	4.00	22.40

4.1 Ash Content

The ash content of a sample is the non-volatile inorganic matter of a compound which remains after subjecting it to a high decomposition temperature. During heating, the organic compounds are decomposed or released leaving behind the residue which consists mainly of other inorganic matters. Hence the ash content can be considered an indication of clean processing. Modification by cross-linking decreases the ash content of starch (Alejandro, et. al., 2008). This trend is obtained from the results of the ash content of the modified starches shown in Table 1; indicating that modification by cross-linking produces cleaner starches. However the neutralization of sodium acetate with adipic acid increased the ash content.

4.2 pH.

The pH of a substance is the degree of acidity or alkalinity of that substance. Starch pastes from cross-linked starches have been reported to be less likely to break down with extended cooking times and possess increased acidity or severe shear (Langan, 1986). Modification increased the pH of the native starch from 5.41 to 5.66, 7.05, 7.13 and 7.54 for modification with sodium acetate neutralized with adipic acid, ammonium phosphate, sodium acetate neutralized with fumaric acid and sodium acetate respectively. It is necessary that the pH of starch tends towards neutrality so that it can be used in industries where a change in the pH of products is not desired. This, modification by cross-linking achieved with improved pH values of the native starch to desirable limits of neutrality.

4.3 Moisture Content

The moisture content of starch is the amount of moisture present in it. The higher the moisture content the lower the amount of dry solids in the flour. The maximum allowable limit for moisture in starch flour is 14% (Austin, 1984). Higher values promote growth of organisms which causes odours and off-flavour. Table 1 show that modification by cross-linking increased the moisture content of the modified starches except for

native starch modified with sodium acetate with a decrease. Mahmut and Sosulski (2004) and Huang et., al (2007) had earlier reported increased water absorption ability of modified starches. Starch modified with ammonium phosphate and sodium acetate mixed with adipic acid had the highest moisture content of 15% and 14.55% respectively, the moisture content in the other samples did not exceed the maximum allowable limit

4.4 Gelatinization Temperature

The gelatinization temperature of starch is the temperature at which the starch forms a completely transparent gel. Gelatinization is a process that breaks down the intermolecular bonds of starch molecules in the presence of water and heat and allows the starch molecules to engage more water. This penetration of water increases randomness in the structure of the starch. As expected the stronger the bond between the starch molecules, the higher the amount of heat required to break the intermolecular bond and therefore, the higher the gel temperature (Singh-Sodhi and Singh, 2005). Cross-linking treatment is intended to add intra and inter-molecular bonds at random locations in the starch granule that stabilize and strengthen the granule (Acquarone & Rao, 2003). Hence modification by cross linking increases the gel temperature of modified starches. This trend is shown in Table 1 as all modified starches had higher gel temperatures than the native starch. The addition of adipic acid and fumaric acid respectively to the sodium acetate modified starch reduced the reaction efficiency of the modification as observed in the reduction of their gel temperatures. Similar thermal properties for cross-linked wheat starch were also reported by Choi and Kerr (2004). They indicated that the extent of the changes depends on the botanic source of the starch, concentration; type of cross-linking reagent and the reaction condition (Chel-Guerrero and Betancur, 1998).

4.5 Swelling Power, Swelling Volume and Solubility Of Samples

When an aqueous suspension of starch is heated, as the temperature increases and exceeds gelatinization

temperature, the starch granules become weakened and the intermolecular bonds of the starch molecule become distorted. This enables water molecules to become more attached to the starch molecules. The granules continue to swell as they absorb more water (Gunarantne and Corke, 2007). Cross-linking has been reported to decrease (depending on the type of cross-linking agent and degree of cross-linking) the swelling power, swelling volume and solubility of starches from various sources (Hoover and Sosulski, 1986). All modified starches show a decrease in their swelling power and swelling volume compared to the native starch as shown in Table 1. The solubility of starch is the water binding capacity of the starch. Table 1 shows that the native starch sample has zero percent solubility. This is because the granules have not been tampered with or ruptured. Results from modification by cross-linking in Table 1 show an increase in solubility of all modified starches with sodium acetate modified starch having the highest solubility of 66.67% showing an increased randomness in the structure of the starch and the rupture of the starch granules. The starch modified with sodium acetate neutralized with fumaric acid has the lowest solubility among the modified starches. Singh et., al (2007) also reported a reduction in solubility and swelling of various cross-linked starch systems. They have indicated that the resistance of a cross-linked starch towards solubility and swelling increases by increasing the concentration of cross-linking agent. Wang and Wang

(2003) also indicated that the cross-linkages may reduce the movement of starch molecules, causing reduction in water solubility and water absorption of cross-linked starch.

4.6 Viscosity

The viscosity of a substance is defined as its resistance to flow and increases as temperature decreases or decreases as temperature increases (Coulson and Richardson, 2004). Starch paste viscosity can be increased or reduced by applying a suitable chemical modification (Agboola et al., 1991). Increasing the level of cross-linking has been reported to reduce or may completely prevent granule swelling which results in a decrease in viscosity (Strivastava and Patal, 1973). The viscosity-temperature behaviour of the native and modified starch samples are shown in Figure 2. The results show that modification by cross-linking improved (reduction in viscosity) the viscosity of the native starch. All the modified starches show a decrease in viscosity at all temperatures compared to the un-modified native starch. The viscosity of native starch, ammonium phosphate and sodium acetate modified starches increase as temperature decreases while the modified starches with sodium acetate neutralized with adipic and fumaric acids respectively gave unstable viscosity-temperature behaviour.

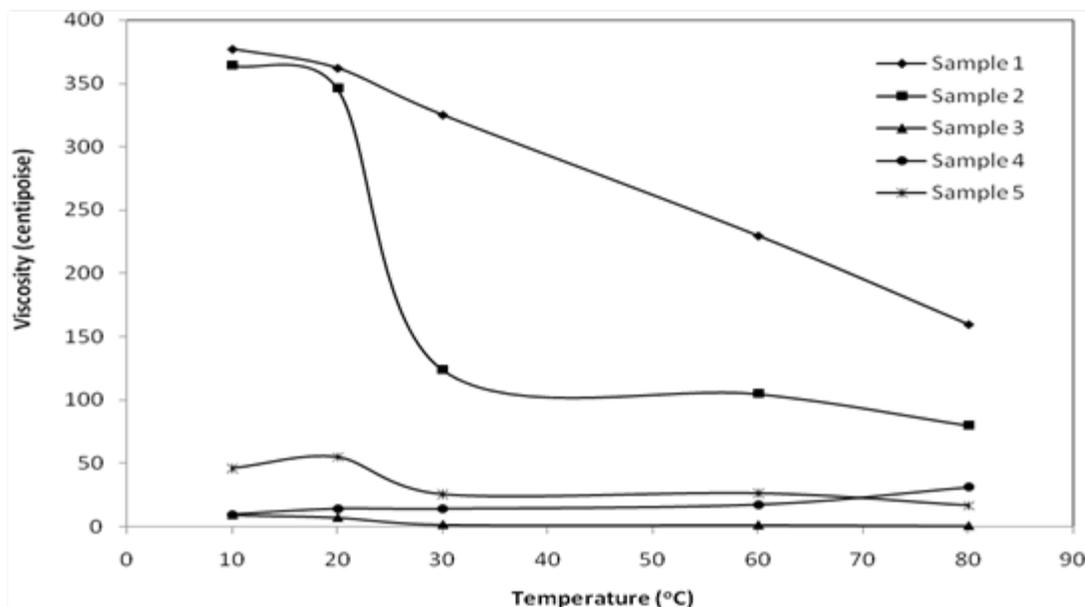


Figure 2: Variation of Native and Modified Starch Samples with Temperature.

5. CONCLUSION

Improvements in the functional properties of a Nigerian variety of native cassava starch were performed.

Modification by cross-linking using four different reagents (ammonium phosphate, sodium acetate, sodium acetate neutralized with adipic acid and sodium acetate neutralized with fumaric acid) was used to produce four grades of modified starches. The modified starches

showed improvements in functional properties such as ash content, pH, moisture content, gelatinization temperature, swelling power (influences texture) and volume, solubility (enhances digestibility) and viscosity.

Starch modified with sodium acetate had the best improvement of the functional properties of the native starch. This starch had low ash content, fairly neutral pH, the highest gel temperature, lowest moisture content and highest solubility. The increased gel temperature gives stronger inter-molecular bonds and makes this starch more resistant to shear stress and retrogradation. All other modified starches showed varying degrees of improvements in most functional properties investigated.

The starch modified with ammonium phosphate also showed an increase in gel temperature, increase in solubility and a decreased starch viscosity with a neutral pH. However, the starch modified with sodium acetate mixed with adipic acid also showed an increase in gel temperature and an increased solubility, the viscosity of this starch sample is quite unstable and has undesirable characteristic for starch to be used in industries. This starch has a pH of 5.66. Starch modified with sodium acetate and fumaric acid has an unstable viscosity, increased gelatinization temperature and solubility. This starch also has a neutral pH of 7.13.

These starches can be used in industries where such starch properties are desired. It is recommended that starch modified with sodium acetate and ammonium phosphate can be used in the paper, paint and adhesives industries because of its resistance to shear stress and low viscosity suitable for surface sizing, coatings and for high quality papers. The increased gelatinization temperature and low viscosity of the modified starches made it also suitable for use in the production of canned foods where retrogradation and syneresis (the release of water from starch after gelation) is not desired.

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