

Full Length Research Paper

Effect of cross linking on the physicochemical properties of cola starch

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Cola starch from *Cola nitida (rubra)* was isolated using 1% (w/v) sodium metabisulphite solution and was chemically modified with sodium tripolyphosphate (STPP) and acetic anhydride (ACOH) as cross-linking agents. The physicochemical and functional properties of the cross linked (modified starch) were compared with the native (unmodified) cola starch. The results presented important changes in the pasting, thermal transition and morphology of the native starch. The morphology of cross linked cola starch appears different from that of the native starch. The shape of the granules appears distorted and the general smoothness of the wall was replaced with some edges. Presence of slight aggregation of the starch granules was also observed. The physicochemical properties of the cross linked starch were obtained as follows: swelling 7.35 to 7.86% for ACOH, 6.00 to 6.20% for STPP, solubility 6.38 to 6.52% for ACOH and 6.23 to 6.48% for STPP, amylose (%): 23.88 for STPP and 24.58 for ACOH while the corresponding values for the native starch were, swelling: 8.85%, solubility: 7.48% and amylose: 24.76%. The results showed a decrease in percent swelling and solubility of cross linked starch compared to the native starch. Comparable values were obtained for both cross linking agents. The Rapid Visco Analyser (RVA) showed that both cross linking agents affected the peak, breakdown, set back and final viscosities of the native cola starch. The peak, breakdown, and set back viscosities of the cross-linked cola starch were lower than that of the native starch, while the final viscosity of the cola starch is lower than that of the cross linked starch. The extent of change is a function of temperature and heating times. The observed trends are consistent with other modified starches that have found useful applications in food and confectionery industries.

Key words: Cross-linked (modified) starch, native starch, isolation, starch modification, physicochemical characteristics.

INTRODUCTION

Native (unmodified) starches have different functional properties depending on the crop source and are considered a primary resource that can be processed into a range of starch products. The limited application of native starches is due to low shear resistance, thermal resistance, thermal decomposition and high tendency towards retro gradation, high syneresis, extreme processing conditions such as pH, temperature etc.,

(Cousidine, 1982). The limitations experienced from native starch may be overcome by various modifications (Jacobs and Delcour, 1998). The basis of starch modification lies in the improvement of its functional properties by changing the physical and chemical properties of such native starch (Ortoefor, 1984).

Starch modification which involves the alteration of the physical and chemical characteristics of the native starch, to improve its functional characteristic can be used to tailor starch to specific applications (Hermansson and Svegmarm, 1996). It is generally achieved through derivatization such as etherification,

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esterification, cross linking and grafting of starch, acid or enzymatic hydrolysis, oxidation or physical treatment of starch using heat or moisture. Of the various modification methods, cross linking is believed to reinforce the hydrogen bonds in the starch granule with chemical bonds which act as a bridge between molecules. As a result, when the cross-linked starch is heated in water, the granule may swell as the hydrogen bonds are weakened, but the chemically bonded cross link may provide sufficient granule stability to keep the swollen granules intact and minimize or prevent loss in viscosity. The modified starches generally show better paste clarity, better stability, increased resistance to retro gradation and increased freeze thaw stability (Zheng and Bhatta, 1999). Cross-linked starches are employed mainly as thickening agents and stabilizers in baby food and high-acid food systems such as sauces and dressings for pizzas, spaghetti, jams and pie fruit filling.

In our earlier work, cola starch was isolated from *Cola nitida (rubra)* spp) and characterized in our laboratory (Omojola et al., 2010). Its physicochemical characterization shows high industrial potentials in the pharmaceutical, food and confectionary industries. The present study is to modify the starch through cross linking using two different cross linking agents, evaluate its physicochemical properties, compare with that of the native starch and other modified starches and suggest possible industrial applications.

MATERIALS AND METHODS

C. nitida rubra spp were procured directly from Kolanut market in Ondo, Ondo State, Nigeria. The nuts were removed from the pods, wrapped in green leaves and kept in a basket at room temperature until required. This is necessary to ensure the retention of the quality of the nuts. Sodium metabisulphite (BDH, UK) was purchased from Zion Chemicals, Abuja. Corn starch (BP) and Analytical Grade Chemicals and reagents were obtained from the Pharmaceutical Technology Department, National Institute for Pharmaceutical Research and Development, Idu, Abuja, Nigeria and Sheda Science and Technology Complex, Sheda, Abuja.

Extraction of starch from *Cola nitida*

The extraction procedure as described in Omojola et al. (2010) was adopted. 5 kg of the *C. nitida (rubra)* was crushed and soaked for one and half hour in 4 L of 1% w/v sodium metabisulphite solution to ensure proper hydration. The soaked nuts were removed and wet milled into homogenous fine paste using a big grinding machine. The fine paste was dispersed in 2 L of 1% w/v sodium metabisulphite solution to form a large solution of starch paste. The solution was filtered using muslin cloth, the suspension was then allowed to settle for 1 h and the supernatant decanted.

The starch layer was washed three times each with 100 ml of 1% sodium metabisulphite acid and at each stage of washing, the suspension was allowed to stand for 2 h for proper sedimentation, after which the supernatant was decanted. The mucilage on the starch layer was scrapped to obtain pure white starch. The starch was air dried at room temperature and pulverized to fine powder with a blender.

Preparation of cross linked cola starch

The method as described by Kerr and Cleaveland (1957) was adopted with modifications. To 10 g each of cola starch in boiling tubes, slurry was made by adding 5 ml distilled water. Also 0.1 M NaOH solutions were added in drops until a desired pH between 8 and 11 was achieved. The slurry was heated for 30 min in a water bath set kept constant at 80°C throughout the heating period, thereafter slurries were made and heated for 1, 2, and 3 h.

After heating and cooling under a water tap for 30 min, the pH of the gel was adjusted between 5 and 6 by adding drops of 0.1 M HCl. Sodium tripolyphosphate (1%) was added in drops with stirring. The dispersion was allowed to mix for at least 5 min, thereafter few drops of distilled water was used to wash the cake three times. The cake was then crumbed and air-dried for 48 h. The previous procedure was repeated using acetic anhydride as another cross linking agent.

Determination of physicochemical properties of cross linked starch

The swelling and solubility profiles were determined over a temperature range of 50 to 95°C according to the procedure adopted from Omojola et al. (2010).

The pasting temperature and viscosity of 12% w/v of the acid thinned starch was assessed using the Rapid Visco Analyzer model RVA-3D made compatible with a computer. The samples were assessed for peak viscosity, trough, breakdown, and final viscosity, set back, peak time and pasting temperature. Gelatinization properties of the samples were characterized using a Netzsch DSC 204 F1 Phoenix (Netzsch, Germany). Nitrogen, at the rate of 20 ml/min was used as purge gas; 2.7 mg of powdered material was sealed in an aluminum pan and heated from 30 up to 400°C at the rate of 10°C per min, followed by a cooling cycle back to 30°C at the same rate. The onset gelatinization temperature (T_o), peak temperature (T_p) and gelatinization temperature at end (T_e) were recorded. A light microscope with a micrometer (Nikon AFX-35DX microscope, Japan) connected to a computer was used to determine the particle sizes at 40X magnification and the photomicrograph recorded.

RESULTS

The morphology of the cross linked sample is shown in Plate 1, and that of the native starch is shown in Plate 2. Table 1 shows the swelling and solubility profiles. The thermal and pasting properties are given in Tables 2 and 3.

DISCUSSION

The morphology of the cross linked starch as shown in Plate 1 appears to be different from that of the native cola starch which is depicted in Plate 2.

The shape of the granules in cross linked starch appears distorted and the general smoothness of the wall observed for the native starch was replaced with some edges. Presence of slight aggregation of the starch granules was also observed. These observations are in accordance with morphological changes in cross linked banana starch (Carmona-Garcia et al., 2009).

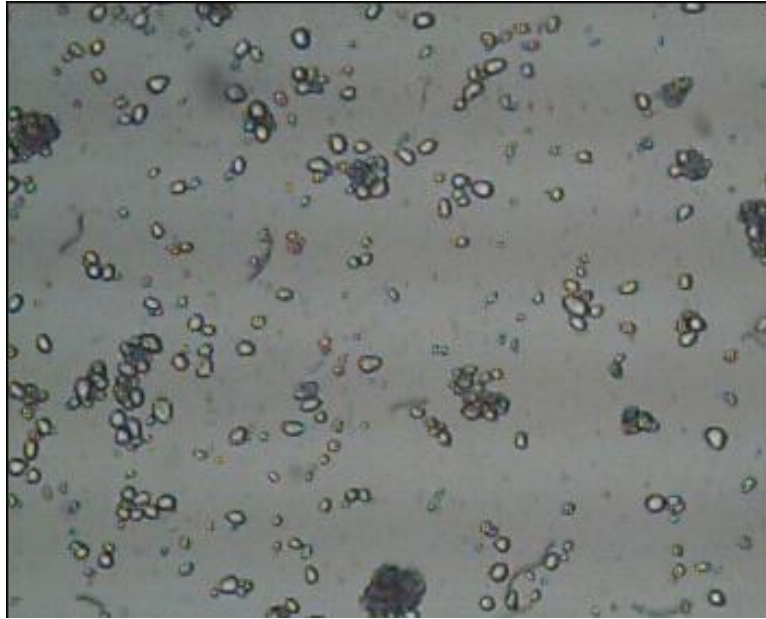


Plate 1. Photomicrograph of native cola starch.

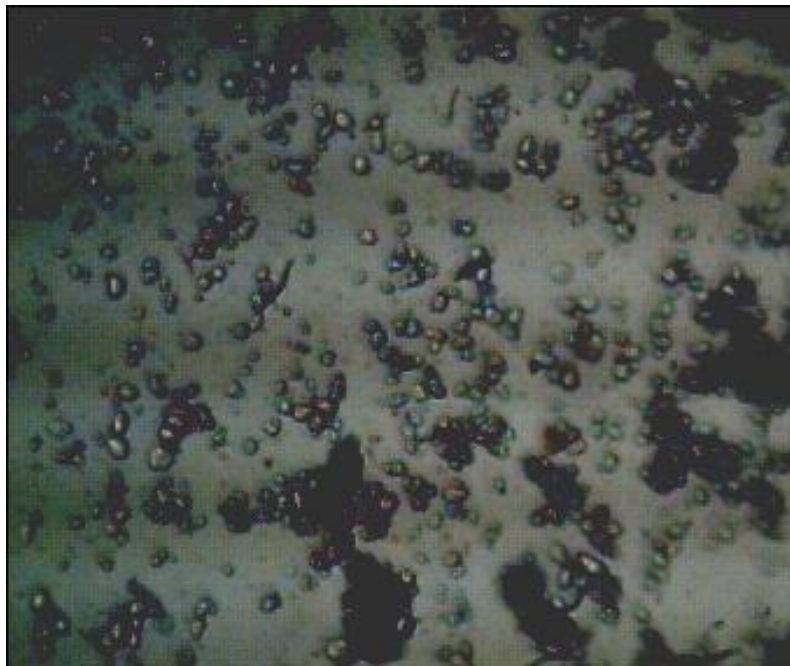


Plate 2. Photomicrograph of cross-linked cola starch using sodium tripolyphosphate (STPP).

The results from Table 1 show that cross linked starches have lower swelling and solubility than the corresponding native starches. The decrease may be due to an increase in cross-link density (Kaur et al., 2004). Cross-linking strengthens the bonding between the starch chains causing an increase in the resistance of

the granules to swelling with increasing degree of cross-linking.

The gelatinization temperature for the acetylated cola starch (cross linked) as shown in Table 2 was observed to be 69.8°C as against 74.0°C for the native starch. Also, the acetylated starch showed lower peak

Table 1. Percent swelling power and solubility of cross linked cola starch.

S/N	Starch	% Swelling	% Solubility
1	Native cola starch	8.85	6.48±0.02
2	Acetic anhydride (ACOH) starch, 2 h- heating	7.35±0.01	6.38±0.01
3	Acetic anhydride (ACOH) starch, 3 h- heating	7.86±0.01	6.52±0.04
4	Sodium tripolyphosphate (STPP) starch, 2 h- heating	6.00±0.01	6.48±0.02
5	Sodium tripolyphosphate (STPP) starch, 3 h- heating	6.20±0.00	6.23±0.02

Table 2. Gelatinization properties of cross- linked cola starch.

S/N	Starch	Glass transition temperature T_o (°C)	Peak temperature T_p (°C)	End set temperature T_e (°C)	ΔH (Te-To)	Pasting temperature (°C)
1	Native starch	301	321.1	340	39	74
2	Acetic anhydride (ACOH) starch	49.8	272.2	67.0	17.2	69.80

Table 3. Pasting properties of cross linked cola starch using sodium tripolyphosphate (STPP) and acetic anhydride (ACOH) as cross linking agents, at different heating periods and temperatures.

S/N	Starch	Peak 1	Trough	Breakdown viscosity	Final viscosity	Set back	Peak time	Pasting temperature
1	Native cola starch	314.42	135.17	179.25	209.58	74.42	4.80	74.50
2	STPP starch, 30 min	220.92±0.01	196.58±0.01	24.34±0.00	290.76±0.00	64.16±0.02	5.53	89.05
3	STPP starch, 1 h	205.07±0.00	167.99±0.02	37.08±0.02	260.16±0.01	62.16±0.02	4.93	88.95
4	STPP starch, 2 h	194.23±0.03	153.33±0.01	40.90±0.02	245.67±0.01	58.73±0.04	5.13	88.20
5	STPP starch, 3 h	189.83±0.01	144.32±0.00	45.51±0.01	237.57±0.01	56.61±0.03	5.00	87.25
6	ACOH starch, 30 min	237.17±0.02	207.85±0.02	29.32±0.02	283.91±0.02	66.07±0.02	5.20	86.70
7	ACOH starch, 1 h	206.74±0.02	174.74±0.02	32.00±0.00	265.32±0.02	64.58±0.01	5.27	89.80
8	ACOH starch, 2 h	197.33±0.00	158.92±0.01	38.41±0.01	249.25±0.01	60.32±0.03	5.13	88.20
9	ACOH starch, 3 h	195.00±0.00	157.68±0.00	39.07±0.00	246.82±0.01	60.17±0.01	5.27	89.80

temperature, T_p of 272.2°C than the native starch of 321.1°C. A lower ΔH was also recorded for the cross linked starch. Table 3 shows the comparative RVA of the cross linked and native starches. The peak, breakdown, and setback viscosities of the cross linked starches are independent of the cross linking agents and are lower than that of the native cola starch. The decreasing trend may be due to the presence of the cross linking agent which may reduce interactions of starch molecules with water molecules resulting in lower peak viscosity values at different time and temperature conditions. The final viscosities however showed a higher value than the native one.

These observations are contrary to other researchers (Gonzalez and Perez, 2000) who reported increased peak, breakdown, setback and final viscosities of acetylated rice starch. The difference may have to do with the nature and structure of starch molecules which vary with starch origin.

Conclusion

The cross linked cola starch showed lower swelling and solubility profiles than its native starch which tend to suggest its use as a thickening agent in food production systems like in soups, jams, conserved sauces, bakery and dairy products. The lower set back viscosity makes it suitable in frozen food applications as a stabilizer.

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