American Journal of Chemistry 2016, 6(3): 80-85
DOI: 10.5923/j.chemistry.20160603.03

Determination of Functional Properties of Acid Treated Acha (*Digitaria Exilis*) Starch Using 36% HCL

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Abstract Acid treatment of acha (*Digitaria Exilis*) starch was carried out using 36% hydrochloric acid in an ethanolic medium. The functional properties of chemically modified sample and the native starch were evaluated: including solubility, water/oil absorption capacity, foam capacity, emulsion capacity, bulk density, pasting property, least gelation concentration (LGC) and starch granule morphology. The pasting viscosity was significantly reduced (50% reduction) on acid treated sample and the least gelation concentration also increased. The emulsion capacity and solubility were increased following acid treatment. But the foam capacity, water / oil absorption capacity and bulk density were reduced on the acid treated sample. Starch granule morphology was investigated using scanning electron microscope (SEM). Increased porous region was observed with the chemically modified sample. The infrared spectra showed similar peaks. Thus, acid treated acha starch possesses potential applications in preparation of low viscosity starch in food, paper and textile industries such as instant soups, stew, gravies sauce, custard, canned food, paper sizing, adhesives, encapsulation of flavor , fats and oil. It also showed promise as a good emulsifying agent.

Keywords Chemical modification, Granule morphology, Retrogradation and seneresis, Least gelation concentration

1. Introduction

In several industrial applications a high content of starch is desired for the starch to form a gel as seen in wine gums and liquorice. When native starch is used as the gelling agent the paste would become too viscous during heating as a very high starch concentration is required to form a gel. In such application acid treated starches are utilized.

Acid treated starches have a low viscosity. In many applications, for example in instant soups, thin boiling starches are often used as filler without any specific technical function. Acid treated starches have been degraded. The most common methods of degrading the starches are oxidation, acid treatment, and enzymatic. Acid treated starches are degraded starches for purpose of low viscosity typical for certain application such as filler in instant soups. When starch is degraded through acid treatment, the glycosidic starch chains are broken almost the way they are when oxidation is used. The difference is that the starch is not stabilized as it is with the oxidation. This shows in a much higher end-viscosity than with oxidation.

The oxidized starch has a much lower end-viscosity than the acid hydrolyzed starch, which is due to the carboxylic acid groups stabilizing the starch in oxidized chemical modification. Acetylation of oxidized starch improves its stability.

When starch is completely hydrolyzed, products such as malto-dextrin, corn syrup, glucose syrup and high glucose syrup have a wide application in the food, textile, brewing, and pharmaceutical industries [1]. These products are mainly derived from corn, barley and potato starch. In Malaysia, sago starch is considered as one of the most important sources of starch. It was reported [2] that about 60 million tonnes of sago starch extracted from sago palms are produced per annum in South-east Asia. However, the raw sago starch exists as large granules with compact crystalline structure. As a result, the enzyme reaction rate and yield of products from raw sago starch was reported to be too low for industrial applications [2].

Bioconversion of sago starch was limited by the resistance of the raw granule to enzymatic hydrolysis. It has been reported that treatment of raw starches with acid at below its gelatinization temperature would enhance its digestibility by enzymes. Therefore, in order to increase the susceptibility of raw sago starch to enzymatic hydrolysis and improve glucose production, sago starch was treated with acid below its gelatinization temperature. The effect of acid treatment on the production of glucose using raw starch as the substrate was studied [3].

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Published online at http://journal.sapub.org/chemistry

Swelling power, solubility and water binding capacity of starches decreased following acid modification. The morphological properties revealed hydrolysis of starch granules is due to attack of acid on amorphous regions, which come in contact with the acid leading to fusion of granules. After modification, starch granules tended to appear fused and less smooth than the native starch granules. The acid modified starches reported slightly higher pasting temperature compared to their native counterparts. The acid modification reduced thickening ability of starches that is based on swollen capacity of undamaged granules as revealed by pasting properties.

Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt. % on dry substance) and amylopectin (65-85 wt. % on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type.

Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1, 000, 000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt. % amylose.

Of some cereal types, such as barley, maize, millet, wheat, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin.

Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are referred to as waxy cereal grains.

For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt. % on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt. % (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

2. Materials and Methods

(a) Sample collection

White Acha grains (*digitaria exilis*) were purchased at a local market in Kubwa, Abuja, Nigeria. The sample was verified by the biological sciences department of Bells University of Technology, Ota, Ogun state, Nigeria.

Preparation of starch slurry

The methods already described [4] with some modification was used. 2kg of winnowed D exillis was steeped in 5 liters of distilled water for 24h at 28℃, after which the solution was discarded and swollen grains, washed with water. The sample was then blended using a domestic milling machine. The slurry obtained was suspended in 5L of distilled water. The slurry obtained was centrifuged at 4500 r.p.m for 30 minutes. The starch obtained was reslurried after centrifugation in 5L of distilled water. The protein was separated from starch using 0.1M NaOH in adjusting pH to between 8.5 and 9.0. An emulsion layer of denatured protein formed was discarded. The process was repeated for the starch slurry until the emulsion layer became less visible. The starch slurry was finally washed with acetone and air dried for 24hours at 28℃.

Acid treatment of starch

The procedure described [5] with some modification was used. 25g of Acha starch was suspended in 100ml of ethanol in a 500ml conical flask. To the starch solution was added 20ml of 36% HCl and reaction allowed to proceed for 1 hour at 45℃ in a shaking water bath. The reaction was then stopped by neutralizing the solution media with 1M NaOH. The slurry was transferred into 50ml centrifuge tube and centrifuged at 3500rpm for 5 minutes. The supernatant collected and the precipitate washed with 50% ethanol until neutral to litmus. The acid treated starch was filtered using Whatman No. 1 filter paper and dried in an oven at 40℃, weighed at room temperature.

Determination of physicochemical properties

Solubility:

The native starch and modified starch samples (2g each) were suspended in 20ml of distilled water. Then heated to 70℃ for 30 minutes with continuous shaking. The mixture was then centrifuged at 4000 rpm for 15 minutes. An aliquot of supernatant (5ml) was evaporated at 105℃ and weighed. The solubility of starch is the ratio in mass (g) of the dried supernatant to the initial mass (g) of dried starch [7].

(b) Water and Oil absorption capacity

1g of native and modified starch were weighed into test tubes. 10ml of distilled water (and 10ml of groundnut oil in the second test tube) were added, and then heated in a water bath at 60℃ for 30 minutes. The starch slurry was centrifuged at 1000rpm for 15 minutes and the supernatant carefully decanted and the weight of the starch paste taken.

WAC/OAC= weight of starch paste/weight of dry starch sample [7].

(c) Bulk densities of native and modified starch

2 grams each of native Acha starch and the modified starch were placed in a 10ml measuring cylinder and the volume occupied by the sample without tapping recorded. The bulk density is the ratio of the weight to volume occupied [7].

(d) Least gelation concentration of starch

The method described [7] with some modification was used. Eight samples each for native and modified starches (1-16% w/v) were prepared in test tubes with 5ml of distilled water. The starch solutions were mixed using magnetic stirrer for 5 minutes and heated for 30 minutes at 80 ℃ in a water bath followed by rapid cooling under running cold water. Further cool at 4 ℃ for 2 hours. Least gelation concentration was determined as that conc. when the samples from the inverted test tube did not fall down or slip.

(e) Pasting properties of the starch

Pasting properties of the native starch and modified sample was carried out using Brookfield viscometer**.** Readings were taken after 10 revolutions each.

(f) Foam capacity of starch

2 grams of native Acha starch and each of modified starch were homogenized in 100ml of distilled water using a magnetic stirrer for 5 minutes. The homogenate was poured into a 250ml measuring cylinder and the volume occupied was recorded after 30 seconds. The foam capacity is expressed as the percent increase in volume [7].

(g) Emulsion capacity of starch

2g of native and modified acha starch were dispersed in 25ml of distilled water using a magnetic stirrer for 30 seconds. After complete dispersion, 25ml of vegetable oil (groundnut oil) was added gradually and the mixing continued for another 30 seconds. Then centrifuged at 1600rpm for 5 minutes. The volume of oil separated from the sample was read directly from the tube. Emulsion capacity is the amount of oil emulsified and held per gram of sample [7].

(h) Starch Granules Morphology

The starch granule Morphology of both the native starch and modified starch were obtained using scanning electron microscopy (SEM) at 25 kev accelerating voltage and 2500 magnification each

3. Results and Discussions

Physico chemical properties

Solubility

The results of solubility of native acha starch (NAS) and acid treated starch (HAS) are shown on table 1. The solubility expressed as gram per 100 gram of starch (g/100g) increased from 10.24 value observed with the native acha starch to 11.50g for the modified starch. Solubility increased following acid treatment modification. This increase in solubility following acid treatment may be attributed to increase in the hydroxyl groups resulting from the break in glycosidic bond linkages and reduction in molecular weight distributions.

Water absorption capacity

The water absorption capacities of native acha starch and chemically modified sample are presented on table 1.

The reduction in water absorption capacity of acid treated sample might be due to increase in starch crystallinity that probably restricted the access of water into the starch granules of the acid thinned starch. This result was in agreement with [4] the observations reported on water absorption capacity of modified bambara groundnut starch.

Table 1. Functional properties of native and modified starch

Functional Properties	NAS	HAS
Solubility (9)	10.24±0.02	9.32±0.04
Water absorption Capacity (%)	488	315
Pasting viscosity cP Oil Absorption	31.5	15.1
Capacity (%)	122	112
PH of Starch	6.85	7.80
Bulk density (g/ml)	0.50±0.01	0.39±0.01
Foam capacity (%)	4.0±0.00	10.0±0.00
Emulsion capacity	36±0.01	40±0.00

Result are mean of triplicate determinations

NAS=Native acha starch; HAS = Acid treated acha starch;

Oil Absorption Capacity

The result of oil absorption capacity of native acha starch and modified sample are presented on table 1. The values expressed as percentage decreased from 122 observed with native acha starch to 112 observed for acid thinned sample. The increase in starch crystallinity restricted access of oil into the granule of the starch.

Bulk density

The bulk density of native acha starch and modified sample are presented on table 1. The bulk density values reduced from 0.50 to0.39 on modified sample. The reduction in bulk density might be attributed to increased crystallinity following chemical modification. Increase crystallinity is characteristic of more ordered state and this might impact greater stability on the modified samples. Thus retro gradation of native acha starch as well as seneresis may be improved upon modification [5]. This improved physical property following chemical modification of native acha starch is desirable in food and pharmaceutical applications as good dispersant and preparation of biopolymer based flocculants.

Foam capacity

The result of foam capacity of native acha starch and modified samples are presented on table 1. The acid treated sample increased in foam capacity from 4% to 10%.

Emulsion capacity

The emulsion capacity of native acha starch and acid treated sample are presented on table 1. The emulsion capacity increased from 36% to 40% in the acid thinned sample. This suggests that chemically modified acha starch are better emulsifying agent due to the increase in hydroxyl groups in the modified starch molecules increasing the binding force of the starch granules.

Least gelation concentration

The gelation properties of native acha starch and acid thinned samples are presented in table 2. The least gelation concentration increased from 6% to 14%. Gelation is a phase phenomenon resulting from aggregation of starch molecules. Since acid treatment of starch led to break in the glycosidic bond linkages of starch molecules leading to increase in smaller molecular weight distribution, significant increase was observed in the least gelation concentration following acid treatment of native acha starch. These values agreed with observation of [6] on acha starch acid hydrolysis.

Table 2. Least gelation concentration (%)

CONCENTRATION%	NAS	HAS
2	Viscous	viscous
4	Viscous	Viscous
6	Gel	Viscous
8	Gel	viscous
10	Gel	Viscous
12	Gel	Viscous
14	Gel	Gel
16	Gel	Gel

Starch pasting properties

The pasting properties of native acha starch (NAS) and modified sample (HAS) are presented on table 1. These are shown as viscosities (cP) at room temperature using Brookfield viscometer.

The pasting viscosities of modified samples were reduced from 31.5 centipoise for native acha starch to 15.1 centipoise for acid treated sample. The pasting viscosity reduced by over 50% on acid treatment modification.

Acid treated starch are often referred to as 'Thin boiling starches', for desired applications where low viscosity is important. In such instances where high content of starch is desirable in order for the starch to be able to form a gel as in wine gums and liquorice the pasting property of native starch would be too viscous during heating. In such applications, we can take advantage of the acid treated samples. Also in instant soups compositions, thin boiling starches are often used as filler.

Starch granule morphology

Starch is stored in most green plants as minute granules in the leaves, stems, roots, fruits and seeds. Such starch is stored traditionally for the future use of the plant. The granule morphology of native acha starch (NAS) and modified sample (HAS) are shown in figure 1. These morphologies were investigated using scanning electron microscopy at 15kv accelerating voltage and 2500 magnification each. Though increased crystallinity is observed on modifications, it is observed that modifications may not have destroyed the shape, appearance and structural arrangements of the starch. The starch granules retain its polygonal shape with sizes ranging from 6 µm to 8.57 µm across all samples.

Starch utilization as a food or feed relate to its physical and chemical properties. The solubility of starch starts with swelling in the gel or amorphous region leaving the crystalline structure unaffected. But with higher temperature, the crystalline region melts or dissolves and the entire crystalline structure are destroyed.

Infra Red Spectra

The infrared (ir) spectra of native acha starch (NAS) and modified derivative (HAS) are presented on figures 2 and respectively. The infrared spectra have similar peaks since there was additional functional group introduced during modification.

Table 3. Infrared Spectra

	Bands	interpretation	NAS	HAS
1.	500cm^{-1} - 760cm^{-1}	Skeletal Stretching Vibration of starch	✓	✓
2.	1614 cm^{-1}	Carbonyl group Stretching vibration	x	x
3.	3600cm^{-1}	Hydroxyl group Stretching vibration Of Carboxylic acid	x	x
4.	3420cm^{-1} - 3538 cm^{-1}	Hydrogen-bonded Hydroxyl group on Starch molecules	✓	✓

NAS = Native acha starch;
HAS = Acid treated acha starch
✓ = presence of band in the starch sample
X = absence of band

Fig 6: Granule Morphology: NAS HAS

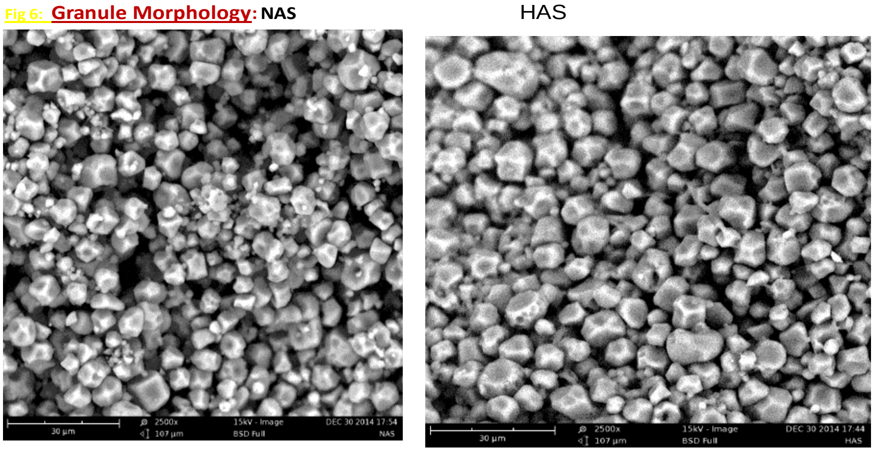

Figure 1. Comparison of Granule morphology NAS vs HAS

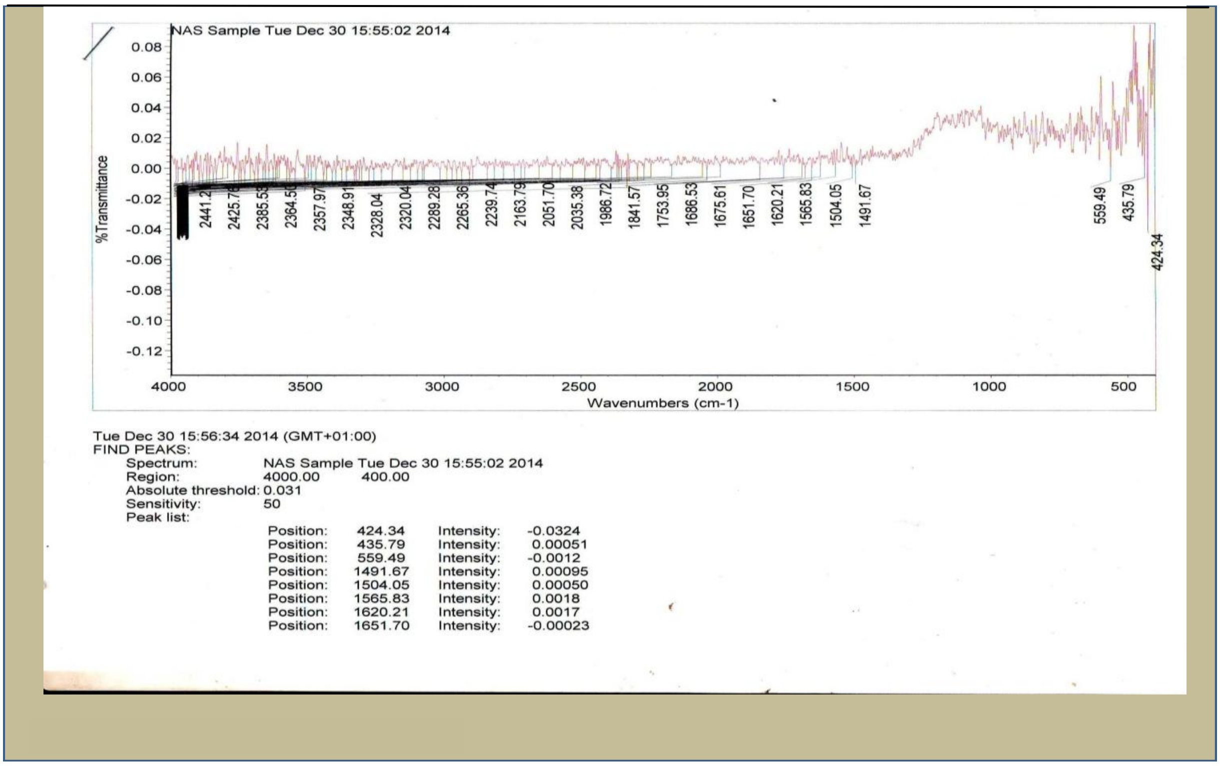

Figure 2. Infra red spectra of NAS sample

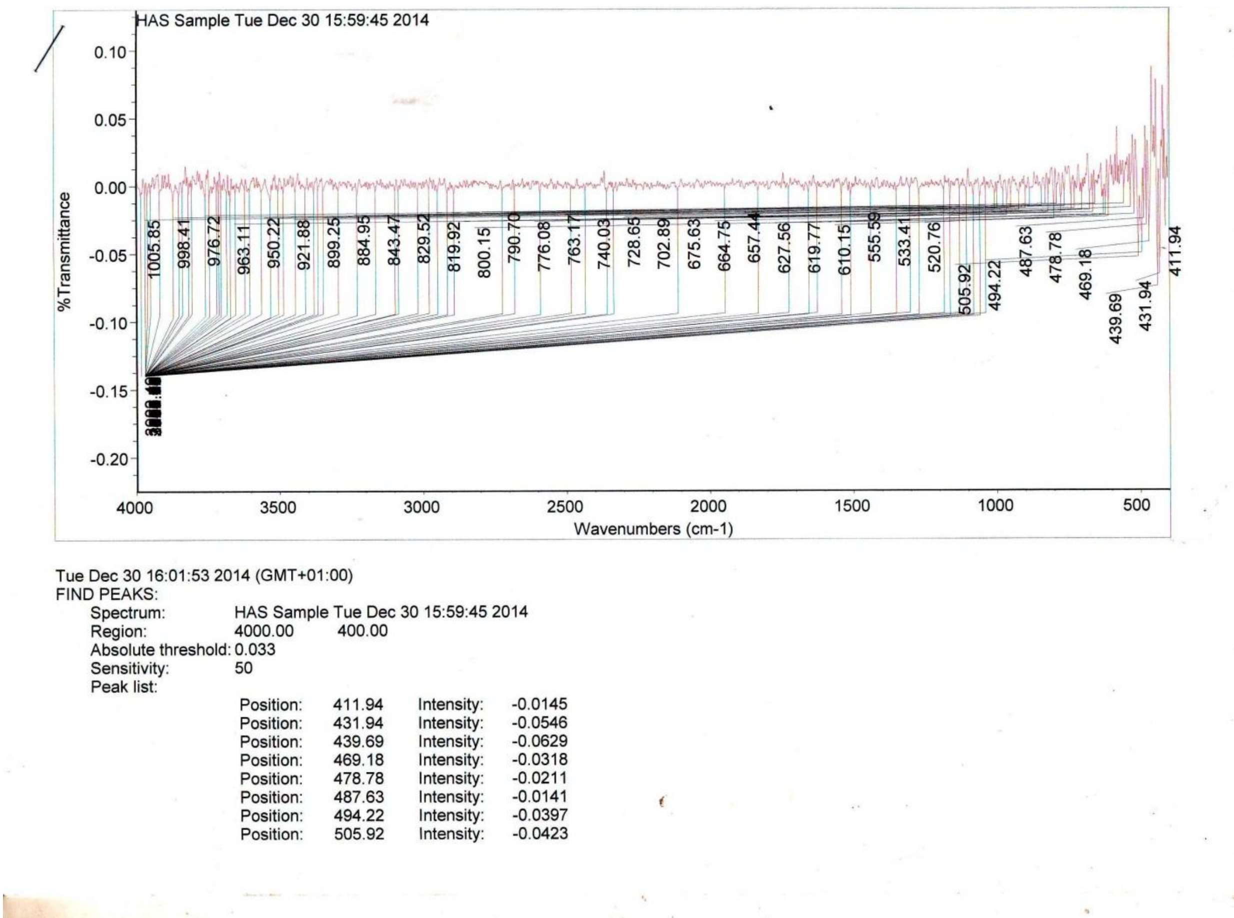

Figure 3. Infra red spectra of HAS Sample

4. Conclusions

Chemical modifications of starch obtained from acha grain were successfully carried out. Physicochemical properties of native acha starch (NAS) and modified derivative (HAS) were determined. Chemical modifications enhanced emulsion capacity. Water and oil absorption capacities, rheological properties expressed as paste viscosities were lowered on modified samples. Potential applications of modified acha starch include good emulsifying agent, starch thickened sauces, soups, paper binding and pharmaceutical drug carriers and disintegrants. Modification improved stability and retro gradation.

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