Journal of Polymer Science and Technology 6(2) 2021:20-26
ISSN: 2550-1917

EFFECT OF pH PARAMETER ON SUCCINYLATED WHITE ACHA (*Digitaria exilis*) STARCH

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ABSTRACT

Acha (*Digitaria exilis*) starch was extracted, succinylated using succinic anhydride (9 g/100 g) and the degree of substitution determined. The moisture content differences were determined between native and succinylated white acha starch. The degree of substitution (DS) property increased appreciably as the pH of the reaction increases. Maximum DS of 0.36 was observed at pH 10. The moisture content for NAS (Native Acha Starch) and SAS (Succinylated Acha Starch) determined were 19.32% and 13.60% respectively. The FTIR spectrum revealed new band in the succinylated starch at 1552.20cm^{-1}, which is attributed to the carboxyl functional group vibration. Succinylated White Acha starch, therefore holds great promise as a good and cheaper replacement for gums in food applications.

Keywords: Acha; *Digitaria exilis;* succinylated scha; starch; moisture content.

INTRODUCTION

Starch is a naturally occurring polymer with wide applications in the food and processing industry due to its safety, biodegradability, inexpensiveness [6], and specific technological properties, such as gelling, thickening, film forming, fat mimicking, etc. [3]. Starch is a carbohydrate with a large number of glucose units joined by glycosidic bonds. It is the most common carbohydrate in human diets and is contained in large amounts in such staple foods as yam, potatoes, wheat, maize (corn), rice, and cassava. Most green plants produce starch as an energy store.

Pure starch is a white, tasteless and odorless powder that is insoluble in cold water or alcohol. It consists of two types of molecules; the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 30% amylose and 70 to 80% amylopectin by weight.

Starch is mainly extracted from cereals (wheat, corn, rice) and from tubers (potatoes, yam). It is stocked in seeds or roots and represents the main plant energy reserve. Starch is the major polysaccharide reserve material of photosynthetic tissues and of many types of plant storage organs such as seeds and swollen stems. The principal crops used for its production include potatoes, corn and rice. Many other starchy foods are grown such as Acha, bananas, barley, breadfruit, millet, oats, sorghum, sweet potatoes, and yams, and many kinds of beans, such as favas, lentils, mung beans, peas, and chickpeas. Native starches, irrespective of their sources are undesirable for many applications because of their inability to withstand processing conditions, so there is a need to improve desirable functional properties.

Figure 1 Pure starch [4]

In order to meet the requirements of specific industrial processes, starches are modified chemically by degradation, substitution or cross-bonding. Chemical modifications improve the functional characteristics of the starch and tailored it to specific food applications. They also offer a number of desirable properties such as high viscosity, better thickening power, low gelatinization and retrogradation.

Chemical modification is generally achieved through derivatization such as etherification, esterification, cross-linking and acid hydrolysis. In acetylation, hydrophilic hydroxyl groups are substituted with hydrophobic acetyl groups. It makes starch more hydrophobic and prevents the formation of hydrogen bonding between hydroxyl groups and water molecules. Since an aqueous starch dispersion has the tendency to increase in viscosity on cooling and finally gel is related to the association of amylose molecules. The acetylation treatment retarding or eliminating retrogradation will affect stabilization of the starch sol.

Acha (*Digitaria exilis*), also known as Fonio, Findi, Hungry rice and Petit mil, is a small seeded cereal, indigenous to West Africa, which is generally classified amongst the millets. Acha is grown in various parts of Nigeria, Sierra Leone, Ghana, Guinea Bissau and Benin Republic on poor sandy soils which could not sustain the growth of other, more demanding cereals. Acha grain is surrounded by an outer protective covering (husk) which is a non-pozzolonic material with specific gravity value of 2.12 is produced by the calcination of the husk [9]. The 1000-kernel weight of acha determined by Jideani and Akingbala [7] indicates that acha is one of the smallest cereal grain. The decorticated seeds of acha are a staple food in some restricted areas in Africa. They are consumed mostly whole, but they are also milled into flour and they constitute a versatile raw material, which can be processed into a variety of preparations such as gruels, porridges and beverages [7]. Acha starch has good disintegrant and binding properties, as well as good glidant properties. It has continued to be important locally because it is both nutritious and one of the world's fastest growing cereals, reaching maturity in as little as six to eight weeks. It is a crop that can be relied on in semi-arid areas with poor soils, where rains are brief.

Acha as discussed above is cultivated throughout West Africa, is in high demand in English-speaking countries and in the Francophone countries, where they are produced [8]. Acha (exilis and iburu), is included in a list of grains considered as whole grains when consumed in whole form [8, 10]. It is believed that exilis and iburu may have nutraceutical properties, as it is used in some areas for managing diabetes. Value addition and exploitation of Acha (exilis and iburu) in the development of health or speciality foods like acha-bread, biscuit, cookies, sour dough, traditional drinks, non-fermented, steamed and granulated dumpling products are gaining interest. These grains may also contribute in addressing some very relevant challenges in today's food formulation—both from functionality and health perspectives [8].

In acid modification, the hydroxonium ion attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage. An acid acts on the surface of the starch granule first before it gradually enters the inner region. It changes the physicochemical properties of starch without destroying its granule structure and the properties of acid thinned starches differ according to their origin [5]. Various studies of the effect of different acids (HCl, HNO_3, H_2SO_4, and H_3PO_4) used in the preparation with similar conditions of treatment on molecular weight, alkali fluidity number, iodine binding capacity and intrinsic viscosity of various starches have been carried out [16].

Starch is hydrophobic, however, succinylation makes starch hydrophilic, as it weakens the internal bonding that holds the granules together [15]. Hence, it modifies its physicochemical properties, which widens its range of applications in food and non-food industries like pharmaceuticals, paper and textile industries. Also, the hydrophobic benzyl groups weakened the internal hydrogen bonding and helped starch swell at relatively low temperature. The aim of this research work is to extract starch from *Digitaria exilis* (White Acha) and, investigate the effect of pH in succinylation of its starch.

EXPERIMENTAL

Materials

A large quantity of dehauled white acha (*Digitaria* exilis) was purchased from Yankaso market, Kano state, Nigeria. Methanol, acetone, isopropyl alcohol, succinic anhydride, sodium hydroxide, toluene, distilled water used were of analytical grade.

Isolation of Acha Starch

Digitaria exilis starch was isolated and purified as described by Lawal [11]. Dehauled 1 kg of acha was steeped in water for 28h at (30±2) °C, after which the steeping solution was discarded and the swollen grains were washed with distilled water. The swollen grains were blended for 30 minutes using electrical blender. The slurry obtained after blending was re-suspended in 5 L of distilled water. It was screened, using a muslin cloth and was for 30 minutes, in which the supernatant was decanted. Starch obtained after decanting was re-slurried in 2 L distilled water and protein was separated from starch by toluene emulsification. Toluene was added (20 mL) to starch suspension and it was thoroughly mixed for 30 minutes and allowed to stand for another 2 hours [11]. An emulsion layer of denatured protein formed at the interface as toluene and water separated and this emulsion layer was discarded. The process was repeated for the starch slurry until emulsion layer became negligible. The starch slurry was then washed with acetone and air-dried for 24h at 30±2 °C.

Starch Succinylation

Starch succinylation was achieved using the method of Awokoya *et al.*, [2]. Starch (100 g) was dispersed in 300 mL of distilled water and stirred magnetically for 1hr. The pH of the slurry was adjusted to pH 9.0 using 1M NaOH. 9g of succinic anhydride was used to treat the starch suspension over a period of 2hr while maintaining a pH range of 8.0 – 9.0. At the end of the reaction the pH of the slurry was adjusted to pH 6.0 using 0.5M HCl. The mixture was filtered, and the modified starch washed six times with distilled water and oven dried for 24 hours at 50 °C [2].

Moisture Content Determination

Petri dishes with lids were washed and dried in an oven. It was cooled to 30°C in a desiccator. Approximately 5 g of starch samples were weighed accurately in petri dishes. The samples were dried for 2 hours at 105°C, cooled in a desiccator and weighed [13]. Moisture content was calculated as shown in Equation (1).

W_1 = weight of petri dish
W_2 = weight of petri dish + starch before heating
W_3 = weight of petri dish + starch after heating

$$\%\ \text{Moisture Content} = \frac{W_2 - W_3}{W_2 - W_1} \text{ X } \frac{100}{1} \quad (1)$$

Degree of Substitution

The method of alkali saponification as described by Arueya and Oyewale [1] was employed for the determination of succinyl content. A sample (1 g) was weighed into a conical flask, 50 mL of 75% EtOH was added, and the mixture was refluxed for 30 minutes while maintaining a temperature of 50°C. After cooling to room temperature, 40 mL of 0.5M NaOH was added. The flask was covered with aluminium foil and allowed to stand at room temperature for 72 hours with occasional shaking. Saponification occurred with the addition of NaOH, and the excess alkali was determined by titrating with 0.5M HCl. Native starch was treated in the same manner to obtain a value for the blank [1]. The percentage of succinyl group and the degree of substitution of the samples calculated using Equation (2) and (3) respectively.

$$\%\ \text{Succinyl} = \frac{(\text{Blanktitre} - \text{sample titre}) \times 0.1 \text{ molarity of acid} \times 100\%}{\textit{Weight of the sample}} \quad (2)$$

$$\text{Degree of substitution (DS)} = \frac{162 \times \%\ \text{succinyl}}{10000 - (99 \times \%\ \text{succinyl})} \quad (3)$$

Determination of pH

10 grams of acha starch was weighed into 15 mL of distilled water and mixed properly. The mixture was poured into boiling distilled water to make up 100 mL of slurry. The slurry was allowed to cool. Using a pH meter (Mettler-Toledo AG 8603), the pH of the slurry was determined.

FTIR Analysis

3 g each of native and succinylated white acha starch were sent for FTIR analysis.

RESULT AND DISCUSSION

Degree of Substitution of Succinylated Acha Starch

The introduction of succinyl groups into the starch structure has greatly influenced the properties of the starch. The succinyl content had a value of 7.84%, while the degree of substitution was 0.12. The degree of substitution generally has a standard value of 3 in which that of the succinylated starch varied between the ranges of 0-3.

Moisture Content

There was a significant change in the moisture content as that of the native acha gave a moisture of 19.32% while that of the succinylated acha had a moisture content of 13.60%, which falls within the 10-20% range recommended for commercial starches.

Effect of pH on the Degree of Substitution (DS) of Succinylated Acha Starch (SAS)

It was observed that degree of substitution is highest at pH 10 while pH 8 has the lowest, this shows a trend that DS increases with pH value in the succinylated starch. Presence of NaOH creates an alkaline environment which enhances degree of substitution. It also facilitates the swelling of starch with an increased surface area for the esterification process.

Table 1 Effect of pH on Degree of Substitution

Sample	pH	DS
SAS 1	8	0.125
SAS 2	9	0.270
SAS 3	10	0.360

FTIR Analysis

The Fourier Transform Infrared (FTIR) spectrum of acha starch showed typical absorption bands of a starch backbone. The absorption bands at 3283.99 cm^{-1} were due to O–H stretching vibration. Usually, absorption range for O–H vibration is 3500–3200 cm^{-1}. The absorption band at 2930.40 cm^{-1} shows the C–H stretching. The weak absorption at 1638.64 cm^{-1} in acha starch probably features the tightly bound water molecules present in starch molecules. Broad absorption bands in the range of 1100–900 cm^{-1} are characteristics of C–O stretching in C–O–C and C–O–H in the glycosidic ring of acha starch.

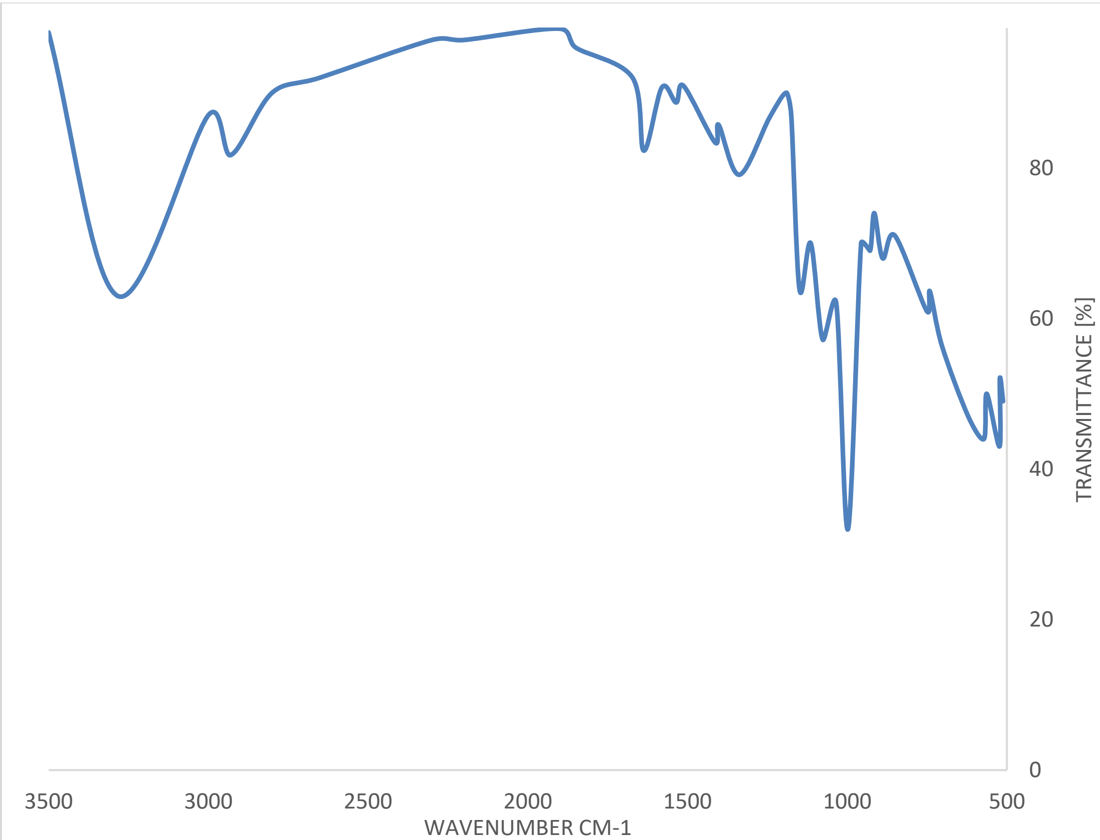

Figure 2 FTIR spectrum of native white acha starch

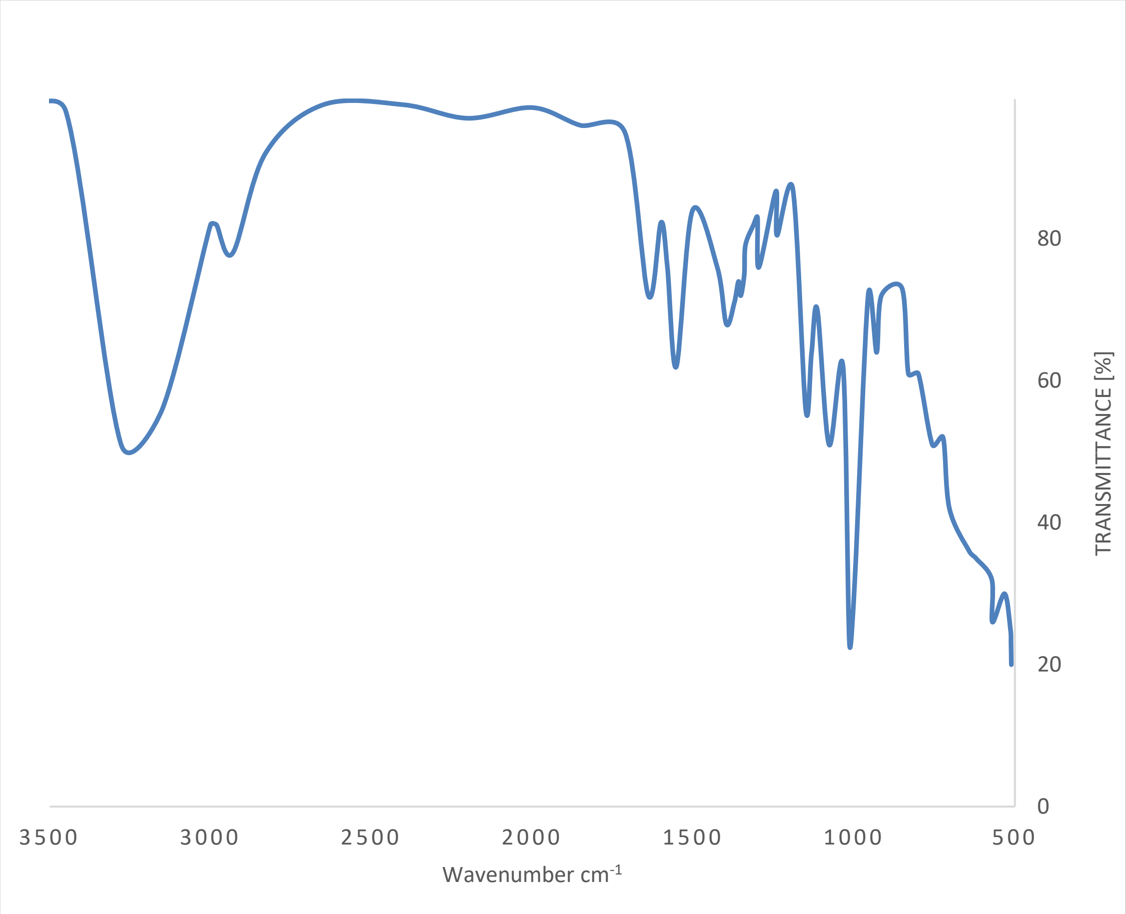

Figure 3 FTIR spectrum of succinylated white acha starch

In the succinylated acha (Figure 3), the absorption band at 1295.59cm^{-1} shows the C–O stretching. Consequently, the vibration of the characteristic carbonyl absorption brought about the new peak in the range of 1552.20 cm^{-1} in the succinylated starch corresponding to the anti-symmetrical and symmetrical vibrations of COO- structure. This shift in the O–H group could be due to the interaction of OH group with the carboxylic group. The reduction in intensity of this band may also be attributed to partly substituted O–H group and the carbonyl group during esterification process.

CONCLUSION

This research work reported the effect of pH on the succinylation of white *Digitaria exilis* starch. The degree of substitution was observed to be pH dependent. Succinylated acha starch exhibited improved functional properties including increased solubilisation in cold water due to the addition of succinic groups which in turn weakens the internal bonding in starch granules. The succinylated acha had a moisture content of 13.60%, which seems to be a good candidate for a thickening agent and stabilizer in food. The aforementioned properties make succinylated acha starch potentially cheaper alternative for application in food systems requiring adhesion of batter to the food and crispy texture after frying. It may make a good replacement for gums in food applications. Thus, succinylated starch is more suitable in food industries.

ACKNOWLEDGEMENT

The authors acknowledge the astute guidance and support of Professor O.S. Lawal of Federal University, Oye Ekiti, Ekiti state, Nigeria; Dr. A.A. Ibikunle of Olabisi Onabanjo University, Ago iwoye, Ogun state, Nigeria; and the entire team members of Todabol Research Group, Lagos state in the execution of this research work.

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