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Physicochemical Analysis of Carboxymethyl Mango (Mangifera Indica) Starch

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Abstract: *The physicochemical analysis of various carboxymethyl starch prepared from my mango seed kernel was determined. The mango seed was obtained from Sokoto local market. After the mango fruit has been consumed, the kernel from removed, the white seed was crushed and grounded to powdered; hot water method was used to extract the starch from the grounded powdered. The extracted mango starch was chemically modified into 15 carboxymethyl mango starch derivatives with Degree of Substitution (DS), and the physicochemical properties determined. The result obtained shows that the Swelling capacity, and Hydration capacity was high for carboxymethyl mango starch with high DS, while the solubility index decreased as the DS increases. The XRD result also shows a loss in crystallinity as the DS increase, the result indicate an increase amorphousness of mango starch due carboxymethylation in alkaline environment.*

Keywords: *Carboxymethyl Mango starch, Degree of Substitution, physicochemical properties,*

I. Introduction

In the rapidly increasing biopolymers industries, starch derivatives play an important role because of its low cost, non-toxic, renewable and compatibility with many other materials for industrial applications. They are used in diverse polymer applications directly or in combination with other synthetic polymers. Starch derivatives were extremely used in food, environmental management, agriculture, pharmacy, biomedical engineering and textile (Ashok et al., 2012).Carboxymethyl starch (CMS), among the derivatives of starch, is one of the most important starch derivatives, synthesized first in 1924 (Finch, 1983). It is also useful for the non-food applications like as paper additives, thickening agent and auxiliary agents in pharmaceuticals (Spychaj, *et al.,* 2013). CMS are white or cream coloured granular starch ethers and esters. Being ethers, they are resistant to cleavage by acids, alkalis and mild oxidizing agents.CMS is obtained by reacting starch with monochloro acetic acid or its sodium salt in presence of sodium hydroxide. The etherification of the OH group of the starch leads to significant change in the properties of starch. It prevents association of the starch molecules. At the same time, the solubility and washing off properties are considerably improved.

Starches can have hydrogen replaced by a different functional group, such as a carboxymethyl group, making carboxymethyl starch (CMS). Adding bulky functional groups like carboxymethyl and carboxyethyl groups reduces the tendency of the starch to recrystallize and makes the starch less prone to damage by heat and bacteria. Carboxymethyl starch is synthesized by reacting starch with monochloroacetic acid or its sodium salt after activation of the polymer with aqueous NaOH in slurry of an aqueous organic solvent, mostly an alcohol. The total degree of substitution (DS), that is the average number of functional groups introduced in the polymer, mainly determines the properties of the Carboxymethylated products (Heinze, 2005).

The functionalization influences the properties of the starch. For example, CMS have been shown to absorb an amount of water 23 times its initial weight. This high swelling capacity combined with a high rate of water permeation is said to be responsible for a high rate of tablet disintegration and drug release from CMS based tablets. CMS has also been reported to be capable of preventing the detrimental influence of hydrophobic lubricants (such as magnesium stearate) on the disintegration time of tablets or capsules (Ochubiojo and Rodrigues, 2012).Though there are many modification techniques, Lawal *et al.* (2007) and Spychaj, *et al.* (2013) have stressed the important physicochemical properties conferred on starches through carboxymethylation which make them more suitable for applications such as disintegrant in drug formulations. Zhou *et al.* (2007) has shown that increase in degree of substation (DS) increases cold water solubility, water absorption capacity, adhesiveness and film forming ability of CMS. Carboxymethylated starch derivatives have also been shown to exhibit lower gelatinization temperature, pH stability and specific changes in rheological properties (Bhattacharyya *et al.,* 1995, Lawal *et al.,* 2007). Tatongjai *et al.,* (2010) equally reported that paste and film clarity as well as paste and gel storage stability of starch improves with carboxymethylation.Our Group had earlier characterized starch extracted from mango seeds and had recently, reported the carboxymethylation of mango seed starch. (Uba *et al.,* 2011)**.** Unlike other common sources of starch such as corn, potato, wheat,

cassava/tapioca and rice (Shah and Augsburger, 2002), there has been no report on the physicochemical properties of carboxymethyl mango starch. Therefore, this paper reports our results on the physicochemical properties of carboxymethyl derivatives of mango starch.

II. Materials and Method

Sample collection and preparation

Ripe Mango was procured from local market (Kasuwar Daji) in Sokoto metropolis, Sokoto State, Nigeria and was identified at the Department of Biological Sciences, Botany Unit, Usmanu Danfodiyo University, Sokoto. The mango was eating with the help of local people and the waste mango seed were collected, washed thoroughly with distilled water, dried, decorticated to remove skin and seed kernel was grounded to powder before extraction.

Extraction of starch

Starch extraction was done using hot water method as described by Uba *et al.* (2011).

Preparation of Sodium carboxymethyl starch

Organic slurry method of modification was employed as described by Lawal *et al.* (2007). The native mango starch (10.0 g) was suspended in 2-propanol (200 ml). 20cm^3 of various concentrations (1.0M, 1.5M or 2.0M) of aqueous sodium hydroxide solution was added. The mixture was stirred at controlled temperature (30°C) for 10 min. 80cm^3 of various concentrations (1.0M, 1.5M or 2.0M) of Sodium monochloroacetate was added and stirring was continued up to the designated time. The pH (Jenway 3510 pH meter) of the mixture was adjusted to about 5.0 by addition of 50% glacial acetic acid and the carboxymethyl starch was filtered, washed with 80% aqueous ethanol until the pH of the liquid is neutral (7.0) and dried in an oven (Nuve Oven/FN-055) at 50°C for 6 hours. The dried carboxymethyl starch was passed through a 100-mesh sieve. This procedure was repeated 15 times with variation in the concentration of SMCA, NaOH, and reaction time and the products of the reactions were labelled CMS-1 to CMS-15.

Determination of the Degree Substitution of sodium carboxymethyl Mango Starch

The degree of substitution (DS) was determined with flame atomic absorption spectrometry based on the sodium content of the CMS as describe by Lawal *et al.* (2009). Each sample (50 mg) was dissolved in concentrated nitric acid (4 cm^3) in a glass vessel and heated with a hot plate. The digested sample was made up to 100 cm^3 with distilled deionized water before analysis with the spectrometer (Corning 400 flame photometer). The flame composition was air–acetylene while the wavelength of sodium was 589.0 nm. The degree of substitution was determined as follows:

$$DS = \frac{162\%\text{Na}}{(2300 - 80\%\text{Na})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

%Na of the unmodified starch was predetermined by flame atomic absorption spectrometry and it was corrected in the CMS derivative.

$$R.E = \frac{DS}{DSt} x\ 100\% \quad - - - - - - - - - - - - - (2)$$

DS of 3 is the maximum any starch carboxymethylation can reach, therefore Reaction efficiency (R.E) is a percentage comparison between the Degree of Substitution(DS) obtainable from the reaction, and the theoretical degree of substitution (DSt = 3) this show the extent to which the carboxymethyl group substitutes hydroxyl group on the starch molecule.

Determination of Physicochemical Properties

Swelling Capacity

This was determined simultaneous as the hydration capacity using the method of Okhamafe*et al*, (1991) and computed according to equation (2).

$$Swelling\ capacity\ (\%) = \frac{V_2 - V_1}{V_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where V_2 is the volume of the hydrated or swollen material and V_1 is the tapped volume of the material prior to hydration.

Hydration Capacity

The method of Kornoblum and Stoopak (1973) was used to determine the hydration capacity of each sample. A 1 g weight of starch was placed in 15 ml plastic centrifuge tube, 10 ml distilled water was added and then closed. The contents were shaken for 2 mins then allowed to stand for 10 mins and immediately centrifuged (TDL-4 Centrifuge machine) at 4000 rpm for 10 mins in a bench centrifuge. The supernatant water was

carefully decanted and the weight of the sediment starch was recorded (Shimadzu/AW320). The hydration capacity of each sample was determined using the equation (1).

$$Hydration\ capacity = \frac{WS}{WD} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where WS and WD are the weight of the sediment formed and weight of the dry sample respectively.

Water Solubility Index (WSI)

The WSI of the starches was determined as described by Anderson and Sefa-dadeh (2001). 2.5 g of each starch sample was weighed (Shimadzu/AW320) into 100 ml centrifuge tube and filled to mark with distilled water and was vigorously mixed, incubated at 37 ^{o}C in a water bath (WBH 6/FL water bath) for 30 mins and centrifuged (TDL-4 Centrifuge machine) at 4000 rpm for 10 mins. The supernatant was collected in pre-weighed beaker and the residue was weighed after the water was evaporated in an Oven (Nuve Oven/FN-055) below 105 ^{o}C. The percentage of residue with respect to the amount of starch used was taken as the water solubility index.

$$WSI = \frac{Wr}{Wd}\ x\ 100 - - - - - - - - - - - - (5)$$

Where Wr = weight of dry residue, and Wd is the weight of sample

XRD Analysis

The X-ray diffraction pattern of native mango starch and its carboxymethylated derivatives were recorded with an X'Pert pro X-ray diffractometer equipped with X'celerator as detector. The diffractograms were registered at Bragg angle (2y) = 10 – 457 at a scan rate of 57/ min and the nature of the spectra was used to confirm the loss of crystallinity of CMS derivatives.

Statistical Analysis

The numerical data obtained from various determinations are averages of triplicate observations. The data were subjected to statistical analysis using GraphPad statistical software (San Diego, USA).One-way Analysis of Variance (ANOVA) at Confidence interval of 95% was used to compare the physicochemical properties of the carboxymethyl derivatives for any significant difference.

III. Results And Discussion

Physicochemical properties of carboxymethyl mango starch derivative

Physicochemical analysis was done on the starches with a view to developing a proper understanding of their swelling power. Swelling is generally accepted as an indication of tablet disintegration ability and can usually be assessed by the determination of parameters such as, hydration capacity, swelling capacity, and water solubility index (Caramella, 1991).From figure 1 and Table 1, it can be deduced that the results obtained show that swelling capacity increases with increase in the degree of substitution (DS) in the modified starches.CMMS 15 was found to have the highest value for swelling capacity while CMMS 1 showed the least swelling capacity, which is directly proportional to their DS respectively, therefore CMMS-15 will have better quality and texture, when used in some consumable products. the increase of Swelling capacity as DS increase, is due to decrease in high proportion of soluble dextrins of small and medium chain lengths in the modified starch granule (John *et al.*, 2002).resulting to an improved capacity of the modified starch to absorbed more water and swell as the DS increases.

Table 1: DS, Swelling capacity, Hydration Capacity, Water Solubility Index, and Powder porosity of Native and Carboxymethyl Starch derivatives.

CMMS Sample	DS	Swelling capacity	Hydration capacity	Water solubility index	Pulse x10[1] (at θ=20)
1	0.039	0.306±0.596	1.019±0.067	1.729±0.134	8.421
2	0.058	0.355±0.019	1.035±0.097	1.256±0.092	8.252
3	0.081	0.368±0.001	1.116±0.129	1.238±0.098	8.212
4	0.099	0.449±0.014	1.166±0.038	1.222±0.110	7.312
5	0.139	0.468±0.004	1.462±0.197	1.221±0.022	7.112
6	0.143	0.488±0.012	1.762±0.040	1.219±0.029	6.516
7	0.156	0.540±0.015	2.011±0.506	1.210±0.102	6.247
8	0.164	0.618±0.011	2.369±0.007	1.128±0.044	6.213
9	0.172	0.942±0.009	2.281±0.090	0.466±0.064	6.111
10	0.184	1.493±0.024	3.103±0.613	0.324±0.048	4.751
11	0.201	1.593±0.007	4.163±0.077	0.306±0.007	4.631
12	0.214	2.002±0.020	4.278±0.054	0.304±0.014	4.375
13	0.258	2.306±0.044	5.552±0.147	0.261±0.024	4.252
14	0.299	2.878±0.033	6.299±0.195	0.252±0.019	1.253
15	0.308	3.217±0.596	6.522±0.265	0.247±0.050	1.122

Table shows mean result ± standard deviation of triplicate analysis.

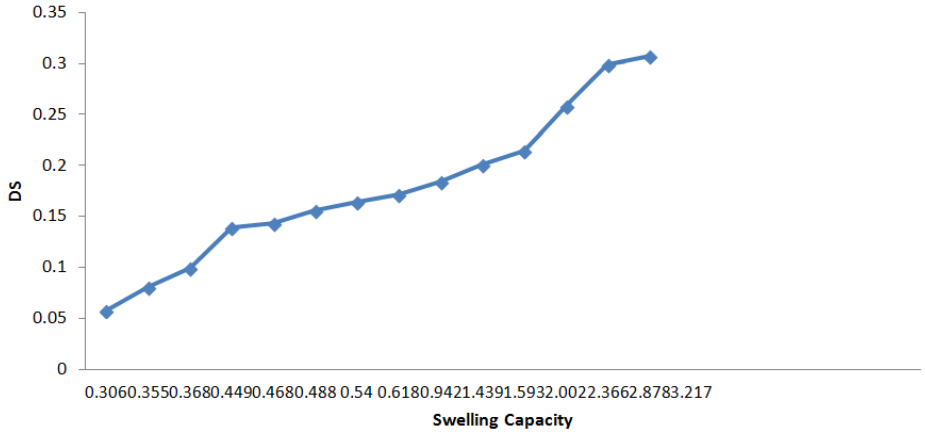

Figure 1: Graph presentation of DS against swelling capacity

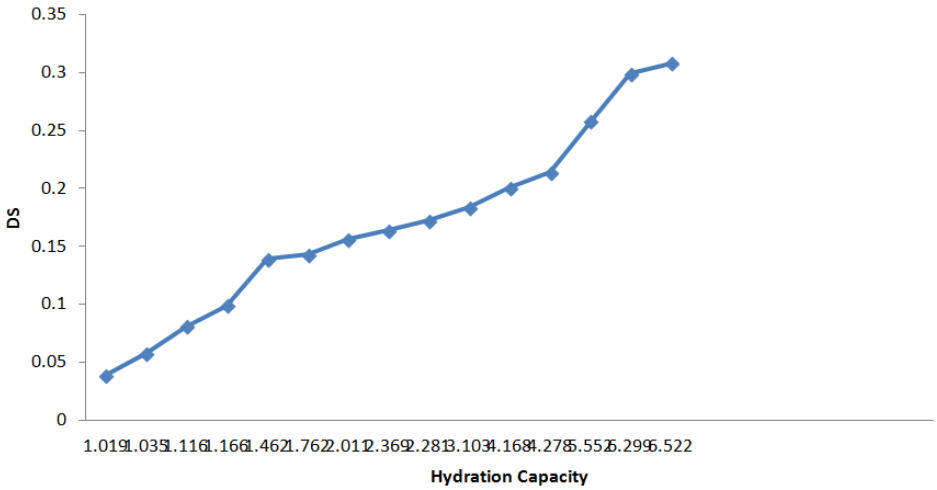

Figure 2: Graph presentation of DS against Hydration capacity

The Hydration capacity refers to the total amount of water held by a starch gel under a defined condition (Hassan *et al.*, 2013). The results obtained showed that the modified starches have better water absorption capacity than the native mango starch (Table 1).Carboxymethylation increases both hydrophilic and hydrophobic capacities of native starch. The carboxymethylation increase hydration capacity because of loss in crystallinity and gain in amorphousness in starch granules that increases the number of available binding sites thus increasing the water binding capacity as shown by Lawal, (2004) and Manmeet-kaur *et al*., (2010)

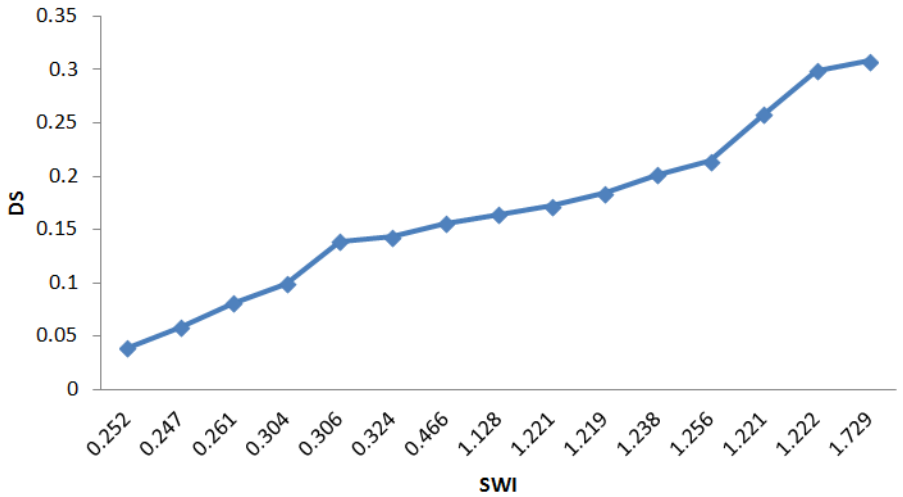

Figure 3: Graph presentation of DS against Water Solubility index (WSI)

CMMS-1 was also found to have the highest water solubility index, which significantly varied from other modified derivatives, and this is because particle of CMMS-1 bind more to water molecules when compared to other carboxymethyl modified starch, and the solubility index decreases as the DS increase (Tijsen *et al.,* 2001) Solubility index of CMMS-1 was higher compared to CMMS-15 (Table 1). Manmeet-Kaur *et al.* (2010) reported that channels present in starch granules may also be responsible for aiding permeation and increase their agents in granules. the hydroxyl groups on the native starch, makes them soluble in water to some extent, but during carboxymethylation, carboxymethylion (CH_3CO-) displaces the hydroxyl group on the starch molecule, resulting to carboxymethyl starch. Carboxymethyl starch particle will not leach away into the water surface due to decreased in the numbers of hydroxyl group on the starch molecules, thereby decreasing its interaction with water. This causes decrease in solubility index of carboxymethyl modified starches.

XRD (X-ray diffractometer MD-10) analysis was carried out on all the samples, the result show that CMMS-15 has the lowest peak which is directly proportional to its DS. X-ray diffractometry of native mango starch and CMMS-1-15 are presented in table 1 and figure 2. The diffractograms (Figs. 4 and 5) and Table 1 reveal more rough peaks, with the highest point 8.422×10^1 pulse for the native starch, whileCMMS-15 highest peak at $2\theta=20$ is 1.122×10^1 pulse. This show a significant difference of 7.30×10^1 pulse between the native and modified starches as observed in the water binding capacity. Less high peaks indicates a loss in crystallinity and an increase in amorphousness due to carboxymethylation which support the result obtained for Hydration capacity. This is not unexpected as Lawal *et al.,* (2007) has earlier reported loss in crystallinity of cocoyam starch due to carboxymethylation. This loss in crystallinity could be attributed to the effect of the alkaline environment and water during the modification because when starch derivatives are treated in an acidic medium the opposite result were obtained by Manmeet-Kaur *et al.,*(2010). In other words, reduction of crystallinity, and increases in amorphousness of the modified derivatives of starch results to significant increase in swelling properties compared to the native mango starch. This opens up a potential utilization of carboxymethyl mango starches as superabsorbent because amorphous granules would enhance water absorption due to increased waters binding capacity. The native mango starch also exhibited an *A-type* crystallinity pattern (Kittiphoon, 2012), (Lawal *et al.,* 2007).

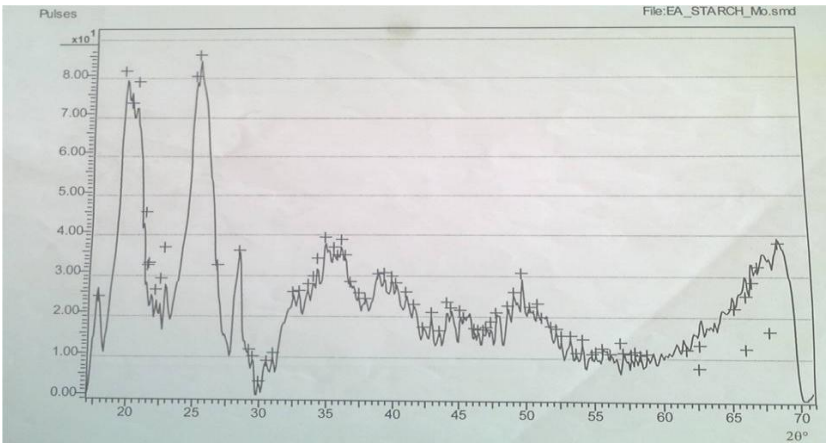

Figure 4: XRD spectrum for Native Mango Starch

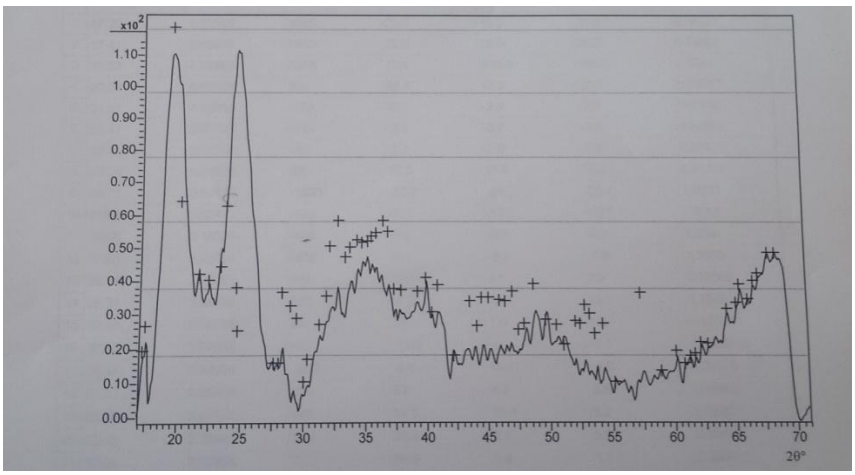

Figure 5: XRD spectrum for Carboxymethyl mango starch (CMMS-15)

IV. Conclusion

The research work indicates that the total physicochemical properties of carboxymethyl starch, depends completely on its degree of substitution. Generally the Carboxymethyl mango starch show an increase of swelling capacity, and Hydration capacity with a decrease of Solubility index, and Pulse as the DS increases. The potential of a novel polymeric biomaterial based on carboxymethyl starch mango and cannot be over emphasize, as report by Sen and Pal (2009) shows the benefit of carboxymethyl starch in controlled drug release analysis. This will open up the use of mango seed starch as a potential unconventional source of starch for pharmaceutical and non-pharmaceutical application.

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