

## Physicochemical properties of *Carica papaya* starch enhanced by etherification modification with sodium monochloroacetate

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### Abstract

Starch isolated from *carica papaya* was modified by treatment with sodium monochloroacetate. Proximate analyses revealed that moisture, ash, fat, protein and carbohydrate increased after carboxymethylation. But, percentage fibre content reduced from 11.46% in native starch to 9.69% in carboxymethyl starch derivative. The carboxymethylation reaction was confirmed by the presence of new intense bands at 1600 and 1419  $\text{cm}^{-1}$  associated with the carboxyl and carboxymethyl substituents of the etherifying agent. The starch exhibited higher water and oil absorption capacities following modification and least gelation concentration reduced in carboxymethylated starch but increased in native starch. The blue value of starch-iodine colour complex, and turbidity stability decreased and improved respectively after carboxymethylation. Carboxymethylated starch showed a significantly lower pasting temperature, peak viscosity, trough viscosity and setback viscosity as compared to native starch. Differential thermal analysis results showed that the carboxymethylation altered the thermal behavior of *carica papaya* starch.

**Keywords:** *Carica papaya* starch, etherification, sodium monochloroacetate, physicochemical properties.

### 1. Introduction

*Carica papaya* Linn belonging to family Caricaceae is commonly known as papaya in English, Papita in Hindi and Erandakarkati in Sanskrit. The plant is recognized by its weak and usually unbranched soft stem (Fig. 1A) yielding copious white latex and crowded by a terminal cluster of large and long stalked leaves [1]. *Carica papaya* is cultivated for its fruits (Fig.1B), and it is favoured by the people of the tropics, as breakfast, and as ingredients in jellies, preserves, or cooked in various ways. Also, the juice makes a popular beverage; young leaves, shoots and fruits cooked as vegetable [2]. Proximate analysis of the pulp showed that it contained starch (43.28%), sugars (15.15%), crude protein (13.63%), crude fat (1.29%), moisture (10.65%) and fibre (1.88%). Also, Unripe pulp of *Carica papaya* can be ranked as rich carbohydrate due to its high carbohydrate and starch contents [1, 3, 4].

Starch, a storage form of glucose in plants, is found as insoluble granules in rice, wheat, potatoes, beans, cassava, millet and sorghum.

Starch granules can be divided into two distinctly general structures: branched amylopectin and largely linear amylose [5]. Most starches contain about 10% to 20% amylose and 80% to 90% amylopectin though the ratio can vary greatly.

Starches are of great value and play vital roles in the food and biopolymers industries. But, using starch in its native form is often limited by certain constraints such as poor solubility, high viscosity, low stability to freeze-thawing, syneresis that in some cases make difficult their utilization [6, 7]. Therefore, it is always reasonable to modify starches to improve their functional properties to suit specific industrial application.

The typical approach, to efficiently improve the functionality of starch is therefore a chemical modification which results in altered physicochemical properties by introducing new functional groups in starches [8]. Starches with strongly diversified functional properties relative to the native material, are obtained primarily through chemical modification [9].

And, the main chemical modification methods include; esterification, etherification, oxidation, crosslinking, and grafting or decomposition reactions such as acid or enzymatic hydrolysis [10, 11, 12]. Starch etherification confers greater stability to starches, permitting their use in water-oil emulsion [13, 14]. Various methods can be used to achieve this modification, which includes; hydroxypropylation, etherification and carboxymethylation etherification [15, 16]. Spychaj *et al.*, 2013 [17], reported the carboxymethylation of potato starch using sodium monochloroacetate in isopropanol/water suspension. Several starches from different origins have also been used for the synthesis of carboxymethyl starch and these include; corn, cassava, sorghum, amaranth and rice starches [18,16]. In recent times, various approaches have also been reported for the synthesis of carboxymethyl starch. This includes; carboxymethylation after starch oxidation, carboxymethylation after  $\gamma$  irradiation, and using of various organic solvents such as ethanol, methanol, and isopropyl alcohol [19, 20, 21].



**Figure 1.** (A) *Carica papaya* plant (www.pinterest.com), (B) Sliced and full *Carica papaya* fruits (www.alamy.com)

In addition, El-sheikh 2010 [22] also reported a method to prepare carboxymethylated maize starch with monochloroacetic acid by mild etherification reaction in the presence of a catalyst. Following carboxymethylation in the presence of a catalyst, higher concentrations of the catalyst was found to increase the reaction rate. Although, carboxymethylated starch prepared from different origins have been reported in the literatures, the authors are not aware of any previous publication concerning physicochemical properties and polymer characterization of carboxymethyl starch from *carica papaya*. To fill this knowledge gap, the present study aims to systematically investigate the physicochemical properties and characterization studies of carboxymethyl starch from *carica papaya*.

## 2. Materials and Methods

### 2.1 Materials

Freshly harvested matured but unripe fruits of *Carica papaya* were collected from a local farm in Ile-Ife, Osun State, Nigeria. Sodium monochloroacetate (SMCA) was purchased from Sigma-Aldrich, Germany and used as obtained. Distilled water was supplied by Department of Chemistry, Obafemi Awolowo University, Nigeria. All chemicals used in starch extraction and modifications were of analytical grade.

## 2.2 Starch extraction from *Carica papaya* fruits (CPF)

*Carica papaya* starch was isolated using the method described by Oloyede 2005 [2] with slight modifications. The *Carica papaya* fruits (15.4 Kg) were peeled, washed thoroughly, seed removed and the pulp cut into small pieces, sun-dried and finely powdered with an electric grinder. The powdered material was then stored in a closed vial at 10 °C in the refrigerator for the starch modification in the next process.

## 2.3 Breadfruit starch yield

Starch yield was derived using Equation 1:

$$\text{Starch yield \%} = \frac{\text{Weight of starch (g)}}{\text{Weight of edible portion}} \times 100 \quad [1]$$

## 2.4 Synthesis of carboxymethyl starch (CMS) from *Carica papaya* (CP) starch

The method of Bhattacharyya *et al.*, 1995 [18] was used with slight modification. Starch (50 g dry wt) was weighed and dispersed in 150 ml of ethanol and stirred magnetically for 1 h. Then, 15 ml of 10 % w/v NaOH was added dropwise into the mixture and further stirred for 1 h at room temperature. After stirring for 1 h, 6 g of SMCA was added to the mixture with continuous stirring for another 1.5 h. Then, the mixture was covered with aluminum foil and placed into the hot air oven at 60 °C for 3.5 h. The slurry was subsequently suspended in 100 ml MeOH for 12 h, and neutralized with acetic acid to pH 7 following which the mixture was filtered. Following filtration, the slurry was dispersed again in 80 % methanol and it was washed several times to remove undesirable by products. Finally, the obtained CMS was filtered and dried at 60 °C to constant weight and kept in a dry place.

Absolute values of the DS of CMS products were determined by the standard method ASTM D1439 with slight modification. A 4 g of the dry powder carboxymethyl starch was stirred in 75 ml of 95 % ethanol for 5 minutes. Then, 5 ml of 2 M HCl was added to the dispersion which was boiled and stirred for 30 min. During this process, the CMS which was in sodium form (NaCMS) was converted to the H-CMS (carboxymethyl starch in hydrogen form).

## 2.5 Determination of degree of substitution (DS)

Afterwards, the mixture was filtered and the solid phase was washed four times with 20 ml of 80 % methanol until the solution became neutral with pH test. Lastly, the precipitate was dried at 100 °C for 3 h and left to cool in a desiccator over silica gel for 0.5 h. 0.5 g of H-CMS was dissolved in 30 ml of 1% (w/v) NaCl solution in a 250 ml conical flask and it was titrated with 1 M NaOH. The DS was determined according to equation 2:

$$DS = \frac{n_{\text{NaOH}} \times M_O}{m_c - n_{\text{NaOH}} \times M_R} \quad [2]$$

$$m_c = m_p - \frac{m_p \times F}{100} \quad [3]$$

$M_o$  = molar mass of the anhydroglucose unit = 162 g/mol

$M_R$  = molar mass of carboxymethyl residue = 58 g/mol

$n_{\text{NaOH}}$  = quantity of sodium hydroxide used (mol)

$m_p$  = weight of polymer taken (g)

$m_c$  = corrected weight of polymer (g)

$F$  = moisture (%)

## 2.6. Proximate analysis

Standard Association of Official Analytical Chemistry (AOAC) methods 1984 [23], were adopted for estimating moisture content, total ash, crude protein, crude fat, crude fibre and carbohydrate.

## 2.7. Physicochemical properties

**2.7.1. Least gelation studies:** The method of Coffman and Garcia 1977 [24] was employed with slight modification. Starch dispersions (2-16% w/v) were prepared in test tubes with distilled water (5ml), the starch suspensions were thoroughly mixed for 5 min. Then, the test tubes were heated for 30 min at 80 °C in a water bath, followed by rapid cooling under running cold tap water for 2 h. Least gelation concentration was determined as lowest concentration when the sample from the inverted test tube did not fall down or slip.

**2.7.2. Oil and water absorption capacity:** The method of Beuchat 1977 [25] was used to determine oil and water absorption capacity of the starch with slight modification. Ten milliliter of distilled water or oil (Devon King's Oil, PZ Wilmar Ltd, Lagos, Nigeria, density 0.9 g/mL) was added to 1 g of sample.

The mixture was mixed thoroughly with a Whirlmix mixer for 30 s and allowed to stand for 30 min. Then, the bound water/oil was determined by the change in weight. It was calculated by Equation 4:

$$\frac{\text{Water}}{\text{Oil}} \text{ binding capacity} = \frac{\text{Bound } \frac{\text{water}}{\text{oil}} \text{ (g)}}{\text{Weight of sample (g)}} \times 100 \quad [4]$$

**2.7.3. Swelling power and solubility:** Effect of temperature on swelling power and solubility determination were carried out in the temperature range of 50 – 90 °C, using the method of Leach *et al.* 1959 [26]. A total of 0.1 g of starch samples were accurately weighed and quantitatively transferred into a clear dried test tube and weighed ( $W_1$ ). 10 ml of distilled water was added to the test tube and the mixture was mixed thoroughly with a Whirlmix mixer for 30 s.

The resultant slurries were heated at desired temperatures, variably between 50 and 90 °C for 30 min in a water bath (using temperature regulated water bath). The mixture was then cooled to room temperature and centrifuged at 6000 rpm for 15 min. The residue obtained from the above experiment (after centrifugation), with the water it retained and the test tube was weighed ( $W_2$ ).

$$\text{Swelling of starch} = \frac{W_2 - W_1}{\text{Weight of starch (g)}} \quad [5]$$

Aliquots (5 ml) of the supernatant obtained after centrifugation were dried to a constant weight at 110 °C. The residue obtained after drying the supernatant represented the amount of starch solubilized in water. Solubility was calculated as grams per 100 g of starch on dry weight basis.

**2.7.4. Turbidity:** Turbidity of NAT and CMS pastes was measured as described by Perera and Hoover 1999 [27]. A 1% aqueous suspension of starch, was heated in a water bath, at 90 °C for 1 h with constant stirring. The starch paste was cooled for 1 h at 30 °C, the samples were stored for 5 days at 4 °C and turbidity was determined every 24 h by measuring absorbance at 640 nm against a water blank with a UV-vis spectrophotometer (UV-1800 Shimadzu, Kyoto, Japan).

**2.7.5. Blue value determination (BV):** 0.1 g dry starch sample was weighed into a boiling tube, 1 ml ethanol (95%) was added, followed by 9 ml of 1 M NaOH solution and heated in a boiling water bath for 10 min to solubilize the starch.

The starch solution was cooled and quantitatively transferred into a 100 ml standard volumetric flask and the volume made up to 100 ml mark with distilled water. Then, 2.5 ml of starch solution was taken into 50 ml standard flask; 0.5 ml of 1 M acetic acid was added followed by 1 ml of stock iodine (0.2 g  $I_2$ /2.0 g KI/100 ml) and the solution made up to the 50 ml mark with distilled water. The resulting colour was left for 20 min to fully develop before the absorbance reading was monitored at 620 nm with a UV-vis spectrophotometer (UV-1800 Shimadzu). Iodine solution of same concentration as above but without starch sample was used in the reference cell. The colour of the starch-iodine complex was monitored visually and the blue value was calculated according to the method of Gilbert and Spragg 1964 [28] using the Equation 6:

$$\text{Blue value} = \frac{\text{Absorbance at 620 nm} \times 4}{\text{Concentration (mg/dl)}} \quad [6]$$

**2.7.6. Scanning electron microscopy (SEM):** To determine the surface morphology of the native (NAT) and CMS starches, each starch granule were taken and dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using concise FEGSEM 6100 Zeiss Ultra Plus Germany at an accelerated voltage of 20.0 kV with secondary electrons in low vacuum mode (LV).

**2.7.7. Fourier transform infrared (FT-IR) spectroscopy:** The Fourier transform infrared spectra of the NAT and CMS starches were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer Waltham, (MA, USA) with an AutoIMAGE System in the frequency range 4000 – 400  $cm^{-1}$ .

**2.7.8. Pasting characteristics:** The pasting characteristics of NAT and CMS starches were determined using a Rapid Visco Analyser Super 4 model (RVA). But, the moisture content of the sample was first determined to obtain the correct sample weight and amount of water required for the test. An aqueous suspension of sample was made by dispersing fifteen grams (dry basis) of starch in 25 mL distilled water. A programmed heating and cooling cycle was employed at constant shear rate, where the sample was held at 50 °C for 1 min, heated to 95 °C in 3 min and then held at 95 °C for 2 min.



It was subsequently cooled to 50 °C within 3 min and then held at 50 °C for 2 min. Readings were then displayed on the monitor in a numerical and graphical form and viscosities were expressed in centipoises.

**2.7.9. Differential thermal analysis (DTA):** Thermal characteristics of NAT and CMS starches were determined using a NETZSCH DTA 404 PC instrument. Starch (5 mg, dry weight) was loaded into a 40 µl capacity aluminum pan and distilled water was added with the help of a Hamilton microsyringe to achieve a starch-water suspension containing 70% water. Also, samples were hermetically sealed and allowed to stand for 2 h at room temperature before heating in the DTA. Then, the DTA analyzer was calibrated using indium and an empty aluminum pan was used as reference. Samples were heated from 28 to 400 °C at a rate of 10 K/min.

Onset temperature ( $T_O$ ); peak temperature ( $T_P$ ); conclusion temperature ( $T_C$ ) and enthalpy of gelatinization ( $\Delta H_{gel}$ ) were calculated.

### 3. Results and Discussion

#### 3.1. *Carica papaya* starch yield

The percentage yield of starch shows how much starch is obtained compared to the maximum possible starch mass. The yield of native starch was 19.05% on the basis of the total weight of dry pulp, which is less than 27.5% reported by Kumar *et al.*, 2012 [29]. However, the variation in the *carica papaya* starch contents might be due to climatic conditions, different maturity, and ultimately the fertility of the soil [30].

#### 3.2. Proximate composition of *carica papaya* starch

The result of the proximate composition of NAT and CMS starches, with respect to protein, fat, crude fibre, ash, moisture, carbohydrate and dry matter is presented in Table 1. All parameters studied, except fibre and dry matter increased after carboxymethylation. The moisture content of the starches ranged between 9.98% and 10.15% which were less than 15% upper limit recommended by the British Pharmacopoeia, 2010 [31]. The CMS derivative had higher moisture content, and increase in moisture content after modification could probably be as a result of the introduction of carboxymethyl group which increased the hydrophilic capacity of the derivatised starch.

This observation is consistent with similar reports on bread fruit starch [32,33] and hybrid maize starch [34]. Similarly, ash, fat, protein and carbohydrate content also increased after carboxymethylation, which may have been indicative of different technique of starch purification [35]. *Carica papaya* starch was of high purity (over 90%) and it contained 8.27% to 9.13% of protein, 2.14% to 2.31% fat and 4.16% to 4.47% ash. Lipids and protein are crucial components of starch granules that can alter their functionality greatly: the protein in starch granules is associated with grain hardness, while the lipids can significantly reduce the swelling capacity of the starch paste.

#### 3.3. Degree of modification and blue value determination

The extent of carboxymethylation for various starch granules is mainly influenced by the introduction of carboxyl groups into the starch structure, and is simply expressed as DS [36].

The properties of the CMS is primarily determined by the total DS, and In this present work, the DS of the obtained CMS was found to be 1.77. This result is in line with the findings reported by Bratskaya *et al.*, 2001 [37] for hydroxyl propyl chloride starch. The BV of the CMS (0.885) changed significantly compared to the control NAT (1.372). And, the decrease in BV after modification could be attributed to the change in molecular organization within the starch granules and more importantly the destruction of the helical structure of amylose. Thus, the observed decrease must have been those associated with amylose unit [38].

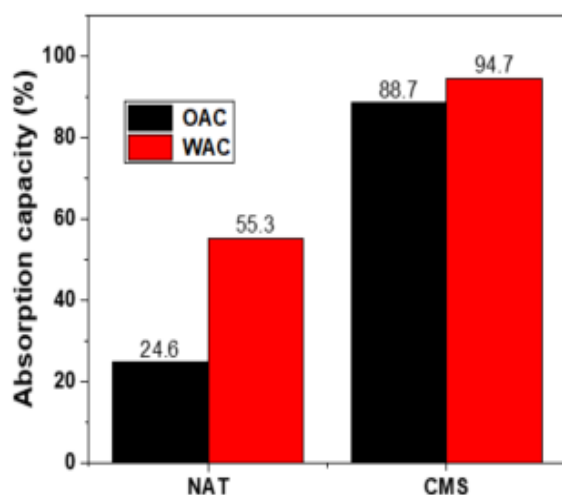
#### 3.4. Gelation properties

Table 2 presents the gelation properties of NAT and CMS derivatives of *carica papaya* starch. The results showed that the NAT starch formed stable gel at higher concentration (14%) compared to CMS derivative and the least gelation concentration (LGC) was used as the index of gelation. The observation illustrated that the LGC reduced after carboxymethylation (12%). Therefore, the lower the LGC, the better the gelation ability of the food [39]. The gel strength of CMS could be attributed to the intermolecular repulsion among the CMS granules which limited interaction of the starch molecule, and which therefore, led to the reduction in gelation properties. In addition, all the starches were liquid at concentrations between 2 and 10%.

### 3.5. Oil and water absorption capacity

Oil absorption capacity is the ability of the dry starch to physically bind fat by capillary attraction which is of great importance, as fat acts as flavor retainer and also extends the shelf life of food particularly in bakery or meat products. Furthermore, restriction of water is an important functional trait in foods such as custards, sausages and dough [40, 41, 42]. Oil and water absorption capacities (OAC and WAC) of the samples are presented in Fig. 1. From this present study, carboxymethylation increased OAC and WAC of the native starch, and both OAC and WAC of the CMS derivative were higher than that of the NAT. This result, suggests that the CMS derivative was more lipophilic due to its higher fat and protein contents, which can enmesh more oil. Similarly, the CMS was also more hydrophilic than the NAT *carica papaya* starch, and this may be attributed to the incorporation of bulky carboxymethyl functional groups which aided percolation and absorption of water within the starch matrices.

This result lends credence to the report of Lawal *et al.*, 2005 [43] that oxidation improve oil and water absorption capacities of hybrid maize starch. Overall, water absorption trends were higher than those for oil absorption which could be attributed to increase in starch crystallinity, and that probably restricted the access of oil into the starch granules.



**Figure 1.** Oil and water absorption capacities of native and carboxymethylated starch of *carica papaya*. Results are means of triplicate determinations. NAT, native *carica papaya* starch; CMS, carboxymethylated *carica papaya* starch

### 3.6. Swelling power and starch solubility

When aqueous suspensions of starch granules are heated, the starch molecule hydrates and swells with a consequent leaching of some soluble starch into the liquid. Thus, swelling power indicates the water holding capacity of starch while the solubility is the percent amount of starch leached out into the supernatant in the swelling volume determination [44, 45]. At the temperature range studied, the results indicated that both swelling power and solubility increased with increase in temperature (Figs. 2 and 3). And, Native starch showed a greater increase in swelling power as compared to carboxymethylated starch.

Therefore, the reduction in swelling power after modification may be due to increase in high proportion of soluble dextrans of both small and medium chain lengths in starch granules [46].

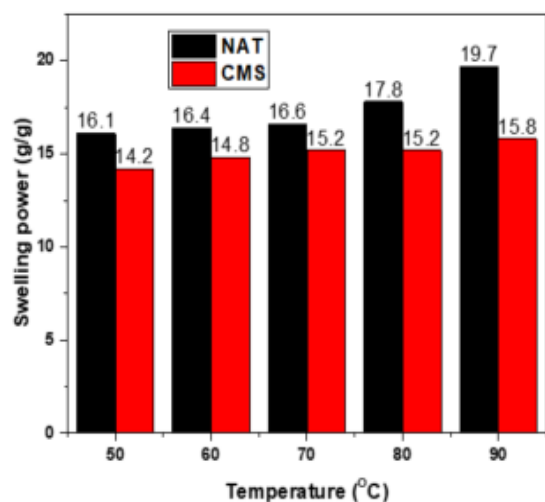
However, solubility increased following modification and it is reasonable, that following introduction of carboxymethyl group on starch molecule, structural disintegration probably weakens the starch granules after modification which, could also be responsible for aiding permeation and thus, enhanced leachates from the starch molecule [34].

### 3.7. Turbidity

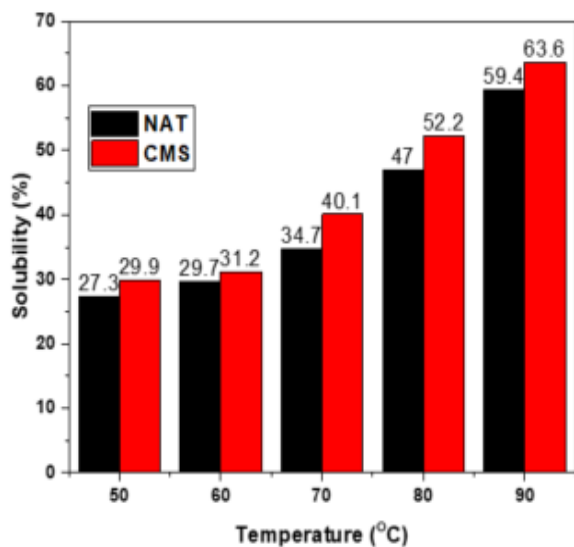
Figure 4 shows the variation in the turbidity of the NAT and CMS derivatives of *carica papaya* starch.

Turbidity values of both the native and carboxymethylated starch suspensions rose steadily with increase in storage period of the starch gels. And, this increase in turbidity during storage in starches has been ascribed to various factors, such as leached amylose and amylopectin, aggregation and crystallization of amylose, granule swelling, lipid and cross-linking substitution [47, 48]. Also, it can be observed that there was no significant change in the turbidity of the native and carboxymethylated starches after the third day.

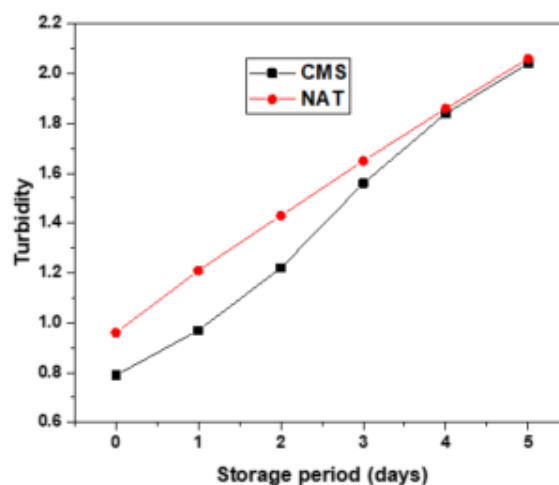
Furthermore, the turbidity values of the CMS suspension in the first three days were significantly lower than the turbidity values of the NAT starch suspension. And, this behavior can be explained by considering the fact that the CMS suspension was more stable than the NAT suspension.



**Figure 2.** Effect of temperature on swelling power of native and carboxymethylated starch of *carica papaya*. . Results are means of triplicate determinations. NAT, native *carica papaya* starch; CMS, carboxymethylated *carica papaya* starch.



**Figure 3.** Effect of temperature on solubility of native and carboxymethylated starch of *carica papaya*. . Results are means of triplicate determinations. NAT, native *carica papaya* starch; CMS, carboxymethylated *carica papaya* starch.



**Figure 4.** Effect of carboxymethylation on *carica papaya* starch turbidity. Results are means of triplicate determinations. NAT, native *carica papaya* starch; CMS, carboxymethylated *carica papaya* starch.

### 3.8. Pasting properties

The transition from a suspension of starch granules to a paste when heat is applied, is accompanied by a large increase in viscosity [40]. Pasting properties of native and carboxymethylated starch derivatives are summarized in Table 3. All pasting parameters, peak viscosity (PV), trough viscosity (TV), breakdown viscosity (BV), final viscosity (FV), setback viscosity (SV), and pasting temperature ( $P_{Temp}$ ) were considerably decreased, following carboxymethylation. Thus, the reduction in PV, TV and SV could be attributed to the rupture of the starch granules [49]. Nevertheless, the effects of modification on TV, FV and SV of starches are often varied depending on the modification, treatment conditions and the botanical sources of starches [50, 51].  $P_{Temp}$  is a measure of minimum temperature required to cook a given starch. Therefore, the decrease in gelatinization temperature after modification could be attributed to weakening and disruption of molecular orderliness within the starch molecule. And, decrease in pasting temperatures following chemical modifications (acetylation and succinylation) have been reported in the literature [34].

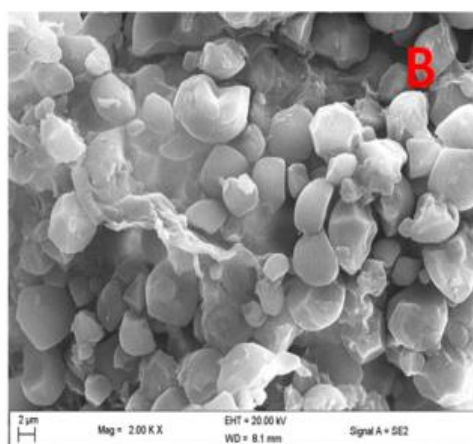
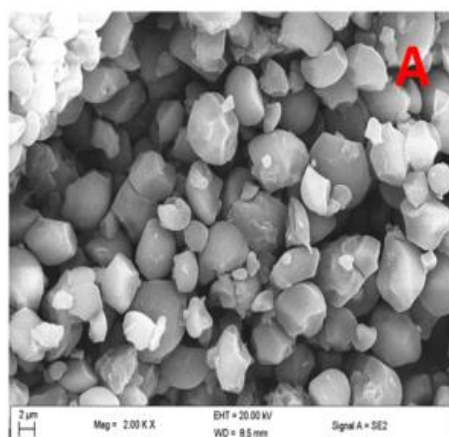
**Table 3:** Pasting properties of native and carboxymethylated starch derivatives of *carica papaya*

Parameter	Starch sample	
	NAT	CMS
PV (cP)	704	682
TV (cP)	698	679
BV (cP)	6	3
FV (cP)	775	746
SV (cP)	77	67
P <sub>Temp</sub> (°C)	95.05	86.35

PV, Peak viscosity; TV, trough viscosity; BV, breakdown viscosity; FV, final viscosity; SV, setback viscosity; P<sub>Temp</sub>, pasting temperature. Values are means of duplicate determinations.

### 3.9. Starch granules morphology

Starch granule size is an important feature that determines the suitability for many of the food and nonfood uses. Starch granule size is highly species-specific and can appear in many different forms such as; polymodal, diverse and polyhedrons [52].



**Figure 5.** Scanning electron micrographs of NAT (A) and CMS derivative (B) of *Carica papaya* starches.

Granule shape and size are also important in relation to their technological properties, including the viscosity of their pastes. The SEM images of the NAT and CMS are shown in Fig. 5. The granule of both derivatives showed a distinctly polymodal pattern. While, the NAT granule surface was smooth with a regular shape, which is characteristic of *carica papaya* starch, the granules of CMS had a considerably irregular shapes with tiny fragments. Fragmentation in the granules of the CMS derivative, could be due to the loss of crystalline structure, as a result of alkaline treatment following carboxymethylation. And this behavior, is consistent with that found by Li *et al.*, 2011 [53].

### 3.10. FTIR

The infrared spectra of NAT and CMS starches are presented in Fig. 6. The bands stretch around 3416 and 3446  $\text{cm}^{-1}$  in NAT and CMS respectively, are attributed to hydrogen bonded hydroxyls on the starch molecules. In the native starch, the band at  $\nu = 1635 \text{ cm}^{-1}$  is assigned to scissoring of two O-H bonds of absorbed water molecules, while the band at  $\nu = 2926 \text{ cm}^{-1}$  is attributed to CH<sub>2</sub> symmetrical stretching vibrations.

The bands at  $\nu = 893$  and  $759 \text{ cm}^{-1}$  are due to skeletal stretching vibrations of starch. Besides, in the carboxymethyl starch, the spectrum showed the typical absorptions of the starch molecule backbone along with the presence of new intense bands at  $\nu = 1600$  and  $1419 \text{ cm}^{-1}$  attributable to symmetric and asymmetric stretching of the  $-\text{COO}^-$  group, indicating the presence of a  $-\text{COO}^-$  group in CMS. According to Pescok *et al.*, 1976 [54], carboxyl groups and its salts show two peaks at the wavenumber about  $1600 - 1640 \text{ cm}^{-1}$  and  $1400 - 1450 \text{ cm}^{-1}$  which indicates the presence of carboxymethyl substituent. In addition, the new intense band at  $\nu = 1247 \text{ cm}^{-1}$  present in CMS spectrum is associated with the C-O symmetric vibration.

### 3.11. Thermal properties

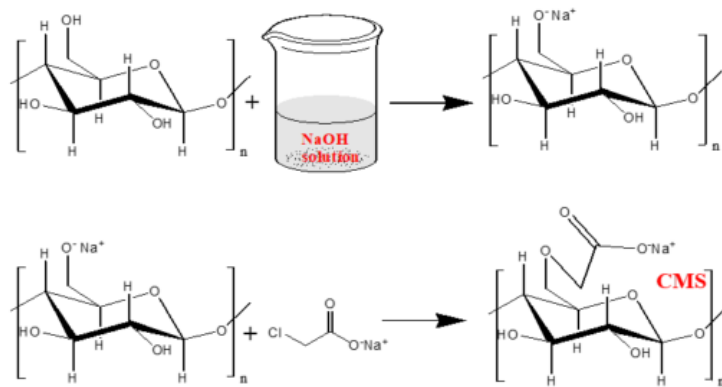
Because polymeric materials are expected to perform under a variety of temperature conditions, thermal properties are important. Thermal property investigations can allow better design of materials that meet the thermal requirements and may also give added structural data. DTA is the most widely applied technique to measure heat of gelatinization of starches.



Thermograms recorded on NAT and CMS starches are shown in Fig. 7. The corresponding gelatinization  $T_0$ ,  $T_P$ ,  $T_C$  and  $\Delta H_{gel}$  are summarized in Table 4. The  $T_0$  and  $T_P$  temperatures of the CMS (86.7 °C and 115.4 °C) were quite higher than those of the native starch (80.2 °C and 113.6 °C). Therefore, the high gelatinization temperature can be due to great degree of crystallite perfection and stability, which was in agreement with previous findings [55]. However, the decrease in conclusion temperature after modification process can be ascribed to the variation of crystallinity.

Enthalpy of gelatinization which represent the amount of energy involved in gelatinization, was observed to increase upon carboxymethylation treatment. The result showed that  $\Delta H_{gel}$  increased from 9.9 J/g in native *carica papaya* starch to 14.2 J/g in CMS sample.

Therefore, the increase in enthalpy with carboxymethylation indicated that a higher percentage of amorphous structure was carboxymethylated and that the molecular order in the modified starch granules had decreased. And thus, agrees with the report of Singh *et al.*, 2006 [44] that acid modification with 1.2% hydrochloric acid increased the  $\Delta H_{gel}$  of sweet potato starch.



**Scheme 1:** Synthesis of starch carboxymethylation with sodium monochloroacetate salt

**Table 1.** Proximate composition of NAT and CMS derivatives of *carica papaya*.

Starch	Protein	Fat	Fibre	Ash	Moisture	Carbohydrate	Dry matter
NAT	8.27	2.14	11.46	4.16	9.98	73.97	90.02
CMS	9.13	2.31	9.69	4.47	10.15	74.40	89.85

All values are means of triplicate determinations

**Table 2.** Gelation properties of NAT and CMS derivatives of *carica papaya*

Concentration (% w/v)	Starch sample	
	NAT	CMS
2	-Liquid	-Liquid
4	-Liquid	-Liquid
6	-Liquid	-Liquid
8	-Liquid	-Liquid
10	-Liquid	± Viscous
12	± Viscous	+Firm gel
14	+Firm gel	+Firm gel
16	+Firm gel	+Firm gel
LGC <sup>a</sup>	14	12

<sup>a</sup>Least gelation concentration.

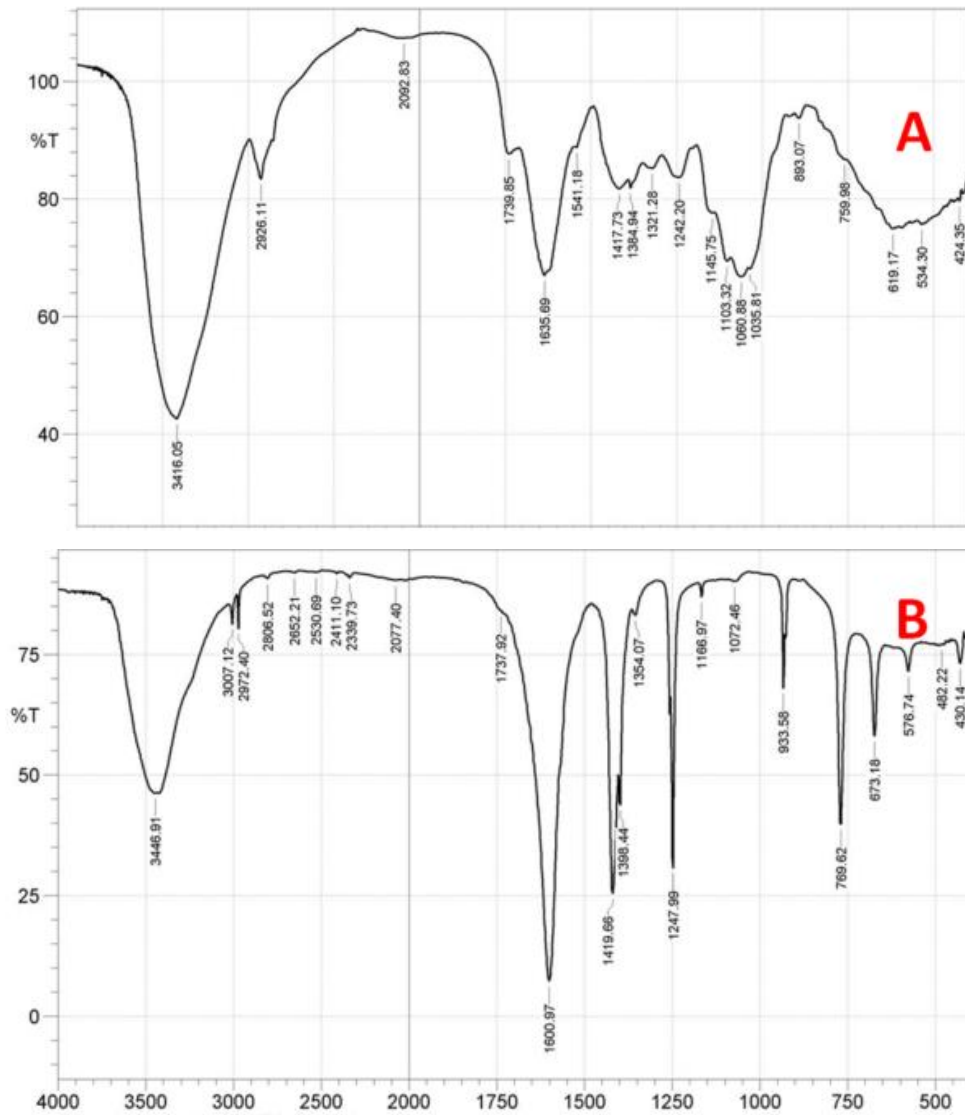


Figure 6. FT-IR spectra of NAT (A) and CMS derivative (B) of *Carica papaya* starches.

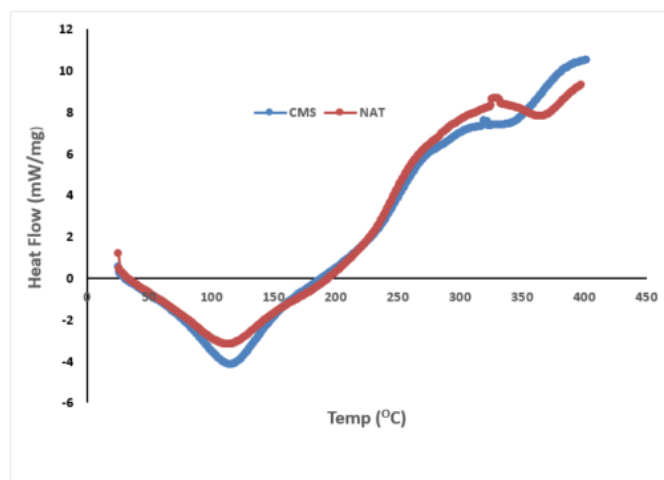


Figure 7, DTA thermograms of native *carica papaya* starch (NAT) and a carboxymethylated *carica papaya* starch (CMS).

**Table 4.** Thermal properties of native (NAT) and carboxymethylated (CMS) *Carica papaya* starches.

Samples	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	ΔH (J/g)
NAT	80.2	113.6	161.2	9.9
CMS	86.7	115.4	152.1	14.2

Also, according to Wang and Wang, 2001 [56], who studied structure and physicochemical properties of acid-thinned potato starch, reported that ΔH<sub>gel</sub> increased following acid-thinned modification.

Similarly, Kim *et al.*, 2012 [57] found that maize starches exhibited higher retrogradation enthalpies with acid hydrolysis.

#### 4. Conclusion

Carboxymethylation of *carica papaya* starch led to changes in physicochemical, pasting, morphological and thermal characteristics of native starch. Also, the *carica papaya* starch has high fibre content and the starch granules appeared to be oval with polymodal pattern. The highest values regarding solubility and the gel strength were found for the modified starch, and the carboxymethylated starch had higher ΔH value because of the decrease in molecular order of the granular structure due to chemical modification. For technical applications, this new carboxymethyl starch derived from *carica papaya* starch appears to have suitable properties for industrial utilization.

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**Compliance with Ethics Requirements.** Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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