International Journal of Food Science and Nutrition
ISSN: 2455-4898; Impact Factor: RJIF 5.14
Received: 26-02-2019; Accepted: 29-03-2019
www.foodsciencejournal.com
Volume 4; Issue 3; May 2019; Page No. 135-140

Effect of cross-linking on structural, chemical and functional properties of corn starch

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Abstract

Cross-linking is a type of chemical modification used to provide desired functional properties. The present study was undertaken to modify and characterize the corn starch treated with ginger and garlic. Corn starch was modified with ginger and garlic and various nutritional, functional, pasting and structural properties were analyzed. Results showed that ginger treated starch increased the degree of cross-linking than the garlic treated starch. Cross linking significantly reduced protein and fat content while amylose content of cross-linked corn starch was increased. Water and oil absorption capacities were not significantly varied between the starches. Cross-linked starches had higher swelling power and solubility than native starch. Peak viscosity was lower in cross-linked starches. Cross-linked starches displayed complex granules with C-type crystallinity. Thus native corn starch could be modified with ginger and garlic to obtain distinctive properties.

Keywords: corn starch, cross-linking, garlic, ginger, pasting properties

Introduction

Starch is a natural semi crystalline biopolymer of D-glucose. The starch molecule is composed of linear amylose and branched amylopectin fractions responsible for its crystalline and amorphous properties (Atichokudomchai *et al*. 2000; Beninca *et al*. 2008) [3, 5]. Starch is one of the most important flexible food ingredient possessing value added attributes for innumerable industrial applications. Its various chemically modified derivatives offer a great scope of high technological value in both food and non-food industries. Oxidation, esterification, hydroxyalkylation, dextrinization, and cross-linking are some of the modifications commonly employed to prepare starch derivatives (Tharanathan 2005) [27]. Acid modification causes degradation of starch without damaging the basic granular size and structure (Lawal *et al*. 2005) [16], although some change in the surface morphology is observed.

The chemical and functional properties achieved, upon modifying starch by chemical substitution, depend on starch source, reaction conditions (reactant concentration, reaction time, pH and the presence of catalyst) (Hirsch and Kokini 2002) [11]. The phosphate diester starches have the phosphate esterified with two hydroxyl groups, very often from two neighboring starch molecules (Nabeshima 2001) [21]. This leads to the formation of a covalent bridge or cross-linking. Phosphate cross-linked starches show resistance to high temperature, low pH, high shear, and leads to increase stability of the swollen starch granule. They improve viscosity and textural properties of the starch. As a thickener and stabilizer, starch phosphate diesters are superior to unmodified starches. They also provide resistance to gelling and retrogradation, and do not synerese on storage. The objectives of present study was to modify the native corn starch with natural cross linking agents such as ginger and garlic and to determine the properties of cross linked corn starches.

Materials and methods

Native corn starch (NCS) was isolated from corn according to the method of Vasanthan (2001) [28]. Ginger and garlic were purchased from local market in Salem, Tamil Nadu. Corn starches were modified with two cross-linking agents such as ginger and garlic according to the method described by Daramola and Osanyinlusi (2006) [9] with slight modification. Ginger and garlic were cleaned, peeled and crushed then mixed with starch-water suspension and stirred periodically for 30 minutes at room temperature. Ginger and garlic grates were sieved and starch milk was washed and water removed using suction pump. The obtained starch was dried using air oven and ground with mortar and pestle to obtain modified starch, namely A (Native corn starch with ginger) and B (Native corn starch with garlic).

Determination of degree of cross - linking (%)

Degree of cross-linking of the cross linked starches was determined from the viscosity values, according to the method of Chatakanonda *et al*. (2000) [8]. The peak viscosities of the starch samples were recorded using a Rapid Visco Analyzer (RVA Tech master, Perten, Instruments Japan). The starch slurry (10% by weight) was heated from 50 - 95 ºC/min at - 12 ºC/min at 160 rpm and then held at 95 ºC for 2 min. Afterwards the paste was cooled to 50 ºC at 12 ºC/min and finally kept at 50 ºC for 2 min. The degree of cross linking was calculated as follows

$$\text{Degree of cross linking} = \frac{\text{A-B}}{\text{A}} \times 100$$

Where, A is the peak viscosity in RV units of the native starch and B is that of the cross-linked starch.

Proximate analyses of samples

Crude protein

Protein content of cross-linked starch was estimated by the method given by AOAC (1990) [1] and using micro-Kjeldahl method.

Crude Fat Determination

Fat content of cross-linked starch was estimated by the method given by AOAC (1990) [1]. The dried sample (1g) was weighed into fat free extraction thimble and plug lightly with cotton wool. The thimble was placed in the extractor and fitted up with reflux condenser and a 250ml soxhlet flask which has been previously dried in the oven, cooled in the dessicator and weighed. The soxhlet flask is then filled to ¾ of it volume with petroleum either (40 – 60°C) and the soxhlet flask extractor plus condenser set was placed on the heater. The heater was put on for six hours with constant running water from the tap for condensation of ether vapour. The set is constantly watched for ether leaks and the heat sources are adjusted appropriately for the ether to boil gently. The ether is left to siphon over several times at least 10-12 times until it is short of siphoning. It is after this is noticed that any ether content of the extractor is carefully drained into the ether stock bottle. The thimble-containing sample is then removed and dried on a clock glass on the bench top. The extractor flask with condenser is replaced and the distillation continues until the flask is practically dried. The flask which now contains the fat or oil is detached, its exterior cleaned and dried to a constant weight in the oven (AOAC 1990) [1]. If the initial weight of dry soxhlet flask is W_o and the final weight of oven dried flask + oil/fat is W_1, percentage fat/oil is obtained by the formula:

$$\text{Fat content} = \frac{W_1 - W_o}{\text{Weight of sample taken}} \times 100$$

Moisture content

Moisture content, dry matter was estimated by the method given by AOAC (1990) [1]. Two millilitres (2mls) of each sample was measured into a previously weight crucible, dry over water for some time. The crucible plus sample taken was then transferred into the oven set at 100°C to dry to a content weight for 24 hour over night. At the end of 24hours, the crucible plus sample was removed from the oven and transfer to dessicator cooled for ten minutes and weighed. If the weight of empty crucible is W0, then, the weight of crucible plus sample is W1. Weight of crucible plus oven dried sample is W3.

$$\text{Moisture \%} = \frac{W1 - W3}{W1 - W0} \text{ x } \frac{100}{1}$$

Determination of Ash content

Ash content was estimated by the method given by AOAC (1990) [1]. Two gram of food sample will be weighed into a crucible. This was transferred into the muffle furnace set at 550°C and left for about 4 hours. About this time it was turned to white ash. The crucible and its content was cooled to about 100°C in air, then room temperature in a dessicator and weighed. The percentage of ash was calculated from the formula below.

$$\text{\% Ash content} = \frac{\text{Weight of ash}}{\text{Original weight of sample}} \text{ x } \frac{100}{1}$$

Amylose content

Amylose content of native and cross-linked corn starches was determined using a colorimetric iodine affinity procedure (Williams *et al*. 1970) [30], briefly a mixture of 0.1 g of the starch sample, 1 ml of ethanol and 9 ml 1 N sodium hydroxide were boiled for 10 min in a boiling water bath and allowed to cool. To a portion (5 ml) of the mixture, 1 ml of 1 N acetic acid and 2 ml of iodine solution were added and absorbance (A) was read using a Spectrophotometer at 620 nm. The amylose content was calculated as:

Amylose content = 3:06 X A X 20;

Where, A = Absorbance value

Functional properties

Water and oil absorption capacity (g g $^{-1}$) (WAC and OAC)

Water and Oil absorption capacity of native and cross-linked corn starches were estimated by the method given by Beuchat (1977) [6]. One gram of the starch sample was mixed with 10 ml of water/oil in a centrifuge tube and allowed to stand at room temperature (30 ± 2°C) for 1 h. It was then centrifuged at 200 x g for 30 min. The volume of water/oil in the sediment water was measured. Water/Oil absorption capacity was calculated as ml of water or oil absorbed per gram of flour.

Swelling power (g g $^{-1}$) and solubility (%)

Swelling power and solubility pattern of native and cross-linked corn starches were studied by the method of Leach *et al* (1959) [17] at a temperature interval of 10ºC from 40-90ºC. In this method, one gram of the starch was suspended in 50 ml of distilled water and kept in a water bath for 30 minutes. The suspension was then removed and centrifuged for 15 minutes at 2200 rpm. Supernatant was allowed to evaporate at 120 ºC and residue thus obtained was subjected to the measurement of percent solubility of starch in water. The swelling power was calculated as weight of the paste sediment per gram of dry starch.

Paste clarity (%)

Paste clarity of native and cross-linked corn starches were determined by Reddy and Seib (1999) [23]**.**

Pasting properties

Pasting properties of native and modified corn starches were measured with Rapid Visco Analyzer (RVA Tech master, Perten, Instruments Japan) (Xiao *et al*. 2012) [31]. Viscosities of starches were recorded with starch suspensions (moisture content 12%, sample 3 g, water 25 ml) that underwent a controlled heating and cooling cycle under constant shear, where the sample was held at 50 °C for 1 min, heated from 50 °C to 95 °C at 5°C/min and held at 95 °C for 2.7 min, cooled from 95 °C to 50 °C at 5 °C/min and held at 50 °C for 2 min. The speed of blending was maintained at 160 rpm. Pasting parameters such as peak viscosity, trough viscosity, break down, final viscosity, set back, peak time and pasting temperature were recorded.

Morphological properties

Granular morphology of the native and cross-linked corn starches were examined by a Scanning Electron Microscopy (SEM). Prior to the examination, native corn starch and cross-linked starch were mounted on a stub with double sticky tape. The stub was then coated with a thin layer of gold in order to improve conductivity and prevent electron charging on the surface. The SEM was operated at 15 kV to image the samples.

Powder X-ray Diffraction (XRD)

X-ray diffraction patterns were obtained by a Powder X-ray diffractometer (Rigaku Mini Hex-II, Japan). Crystallinity Index (CI) was calculated using Equation proposed for cellulose by Segal *et al* (1959) [24] and applied to starch, by using the equation with slight modification:

Statistical analysis

Data were analyzed using one way ANOVA to find out the difference among the native and cross-linked starches in physicochemical and functional properties. All the analyses were done in triplicates.

Results and Discussion

The degree of cross-linking of the cross-linked corn starch was determined from the RVA viscosity values and the results are presented in Table 1. Degree of cross-linking was higher in A sample (39.16 %) than B sample (25.62%). This result is confirmed with Xiao *et al* (2012) [31] who stated that the degree of cross-linking of rice starch ranged from 18.71-72.41%.

Proximate analyses (protein, fat, moisture, ash and amylose) of native and cross-linked starches are presented in Table. 1. Protein content of cross-linked (0.47 % and 0.42%) starches was significantly lower than native corn starch (0.71%). This result is in agreement with the findings of Aparicio-Saguilán *et al* (2008) [2] who stated that the protein content of cross-linked banana starch ranged from 0.53 to 0.55 %. The observed decrease in the nitrogen and protein content of corn starch dextrinized at 200^{0}C was possibly due to protein denaturation. It has been stated from literature (Nakia 1983) [22] that heating above 50^{0}C denatures protein by breaking the non-covalent bonds such as hydrogen, hydrophobic and hydrostatic bonds involved in the stabilization of secondary and tertiary structure.

Fat content of cross-linked starch (0.21 and 0.24 %) was significantly lower than native corn starch. This result is confirmed with Kemas *et al* (2012) [15] who stated that the fat content of modified starches was decreased than native corn starch. Native corn starch was had higher moisture than the cross-linked corn starch. This value is within the (10-20%) moisture level recommended for commercial starches (Soni *et al*. 1993) [26]. The low moisture content is usually reflects the high stability during storage, and it protects starches from mold growth and give a high yield of dry weight. This pattern is related to the reaction between the OH groups of glucose units of starch and the bi- or poly-functional chemical reagent used in this chemical modification, decreasing the possibility of reaction between OH of starch chains and the water molecules and consequently the join of water to this polymer (Carmona-Garcia *et al*. 2009) [7]. Cross-linked corn starch had higher ash and amylose content than native corn starch. This result is confirmed with Yousif *et al* (2012) [33] who stated that modified starches had higher ash content than the native starch. The amylose content of cross-linked corn starch had higher than the native corn starches. Cross-linking reagents might be occurred in the outer regions of the granules and it located on the amylopectin molecules, due to this amylose content may increase (Delval *et al*. 2004) [10].

Water and oil absorption capacity and paste clarity of the native and cross-linked starches are presented in Table 2. Cross-linked starches had lower water (1.13g g^{-1}and1.25 g g^{-1}) absorption capacity when compared to native starch (1.38 g g^{-1}). Cross-linked (1.29 and 1.31 g g^{-1}) starches had lower oil absorption capacity than the native (1.51 g g^{-1}) starch. The paste clarity of cross-linked starch was lower than native starches. This result is confirmed with Xiao *et al* (2011) [32] who reported that the paste clarity of cross-linked starches was lower than native corn starch and it might be due to the larger average granule size of potato starch. Paste clarity is the result of rupture of swollen starch granules, and cross-linking improved the integrity of swollen granules, reducing paste clarity (Zheng *et al*. 1999) [34].

The swelling power of native and cross-linked starches is shown fig1. The results are consistent with the earlier reports (Liu *et al*. 1999; Waliszewski *et al*. 2003) [19, 29]. Swelling power of native starch gradually increased at higher temperature from 40 to 90ºC, but swelling power of cross-linked starch increased up to 80ºC and then it decreased at 90ºC. This result confirmed with Carmona-Garcia *et al* (2009) [7] who reported cross-linked starches had higher swelling power than the native starch and when temperature increased the swelling power of cross-linked starches were decreased. Chatakanonda *et al*. (2000) [8] reported cross-linked banana starch altered the granule structure and the water penetrates easily. The inhibition of swelling as a result of cross-linking is well known (Bea-Young and Yoo 2010) [4] and is attributed to a tight packing of molecules in the granule and a substantial degree on inter-molecular bridging during the cross-linking process. Increasing the degree of cross-linking decreases the ability of the granule to swell and also decrease its viscosity.

The solubility of native and cross-linked starches is shown fig 2. The solubility of the native corn starch was increased with increasing temperature (40–90°C). The cross-linked starches showed higher solubility up to 80 °C after that decreased at 90 °C. Bea-Young, and Yoo (2010) [4] reported that the cross-linked starches had lower solubility than the native starch. Cross-links strengthened the structure of starch granules and prevented the starch molecules from leaching out, so less disintegration took place during gelatinization and the solubility was lower (Hodge *et al*. 1996) [12].

Pasting (RVA) characteristics of native and cross-linked corn starches are shown in Table 3 and Fig.3. The peak viscosity (1008.66 and 1238.33 cP) of cross-linked starches was lower when compared with native starch peak viscosity (1664.66 cP). Native starch (1063.66 cP) had the highest trough viscosity than cross-linked (737.33 and 707.33 cP) starches. Cross-linked starches showed lower breakdown viscosity (268.66 and 531.00 cP) than native (601.00 cP) starch, which could be attributed to the strengthening of the swollen granules against breakage under conditions of high temperature and shear (Jyothi *et al*. 2006) [13]. Final viscosity of cross-linked starches (1219.33 and 1291.00 cP) was significantly lower than the native starch (2058.00cP). The setback value (485.66 and 524.66 cP) of cross-linked starches were lower when compared with the native starch (994.33 cP), Jyothi *et al* (2006) [13] and Xiao *et al* (2012) [31] indicated that the setback values decreased in cross-linked starch. The peak time (5.33 and 4.86 min) of cross-linked starches was higher than the native starch (4.91 min), pasting temperature of cross-linked starches increased in comparison with the native starch. This result is similar to the report of Jyothi *et al* (2006) [13] who stated that the pasting temperature of cross-linked starches had higher than the native starch. The decrease in pasting temperature, peak viscosity and breakdown viscosity of cross-linked oxidized starch could be indicative that higher cross-linking has taken place that is there were sufficient cross-links to retard the swelling of the starch and cause a decrease in viscosity (Kartha *et al*. 2005).

Fig. 4 shows the scanning electron micrographs of the native and cross-linked starches. Native corn starch was composed of granules with round and irregular shape. Starch granules cross-linked with ginger and garlic showed irregular in shape when compared with native starch. Cross-linked starches had more irregular shaped granules than Native corn starch. SEM illustrations showed minor changes in the external morphology with ginger and garlic. As reported by Singh *et al* (2007) [25] slight framentation was noticed in the photographs. Deep grooves in the starch granule were clearly visible for the cross-linked starches. There was no considerable difference between the starch treted with ginger and garli. Neverthless starch treted with ginger have found to have high degreee of exo-erosion compared to starch treted with garlic.

X-ray diffraction

Native corn starch showed a typical C-type pattern with strong reflections at 2θ degrees about 10.62, 11.16, 14.92, 16.82, 17.60, 19.70 and 22.68°. After the cross-linking, the strongest peak at around 11.82, 15.30, 18.20, 20.10 and 23.16° (Sample A) and 11.48, 16.14, 17.78, 20.05 and 23.04° (Sample B) were observed and exhibiting the typical characteristics of a C-type starch. An additional peak at 20.10 was clearly observed and it indicates the presence of V-type crystallinity in the cross-linked corn starch. Lee *et al* (2008) [18]; Mun and Shin (2006) [20] who found that the peak was observed at 20. The starch samples cross-linked by adipic acid and STMP/STPP also exhibited similar X-ray diffraction patterns to the autoclaving-cooling treated corn starch.

Table 1: Nutritional properties of native and cross-linked corn starch

Sample	Degree of crosslinking	Protein (%)	Fat (%)	Moisture (%)	Ash (%)	Amylose (%)
NCS	ND	0.71 ± 0.10^{a}	0.34 ± 0.05^{a}	9.8 ± 0.55^{a}	0.85 ± 0.15^{a}	28.86±2.07
A	39.16±5.47	0.42 ± 0.04^{b}	0.21 ± 0.04^{b}	7.20 ± 1.00^{b}	2.23 ± 0.58^{b}	30.42±1.21
B	25.62±4.73	0.47 ± 0.04^{b}	0.24 ± 0.05^{b}	7.83 ± 0.20^{b}	2.47 ± 0.30^{b}	29.92±0.93
F-value	ND	15.29^{*}	6.37^{*}	12.10^{*}	14.97^{*}	0.86^{NS}
CD value(0.05)	ND	0.13	0.09	1.34	0.78	ND

Mean values superscripted by the same letter are not significantly different within the column. Mean values of three measurements± standard deviation, NCS= native corn starch, A = native corn starch with ginger, B = native corn starch with garlic. CD = Critical Deviation, Degree of cross-linking was tested by using't'- test between A and B samples (t = 3.24), ND =not detected.

Table 2: Water and oil absorption capacity of the native and cross linked starches

Sample	WAC (g g $^{-1}$)	OAC (g g $^{-1}$)	Past clarity (%)
NCS	1.38±0.18	1.51±0.25	43.05 ± 2.75^{a}
A	1.13±0.06	1.29±0.27	36.25 ± 2.97^{b}
B	1.25±0.05	1.31±0.09	35.09 ± 3.82^{b}
F- value	3.34^{NS}	0.91^{NS}	5.35^{*}
CD- value	ND	ND	6.43

Mean values superscripted by the same letter are not significantly different within the column. Mean values of three measurements± standard deviation, NCS= native corn starch, A = native corn starch with ginger, B = native corn starch with garlic. * = Significant at 5%. And NS = Not Significant, CD = Critical Deviation.

Table 3: Pasting properties of the native and cross linked starches

Samples	Peak Viscosity (cP)	Trough Viscosity (cP)	Break down (cP)	Final Viscosity (cP)	Set back (cP)	Peak time (min)	Pasting temperature (°C)
NCS	1664.66 ± 112.34^{a}	1063.66 ± 79.56^{a}	601.00 ± 33.60^{a}	2058.00 ± 164.29^{a}	994.33 ± 84.91^{a}	4.91 ± 0.03^{a}	75.35 ±0.52
A	1008.66 ± 31.56^{b}	737.33 ± 21.07^{b}	268.66 ± 41.42^{b}	1219.33 ± 71.59^{b}	485.66 ± 70.31^{b}	5.33 ± 0.29^{b}	79.7 ± 8.01
B	1238.33 ± 121.13^{c}	707.33 ± 34.12^{bc}	531.00 ± 94.17^{ca}	1291.00 ± 89.60^{c}	524.66 ± 100.30^{ca}	4.86 ± 0.06^{ca}	75.28 ± 0.45
F- value	35.24^{*}	44.28^{*}	23.58^{*}	48.45^{*}	32.46^{*}	6.52^{*}	0.89^{NS}
CD-value	194.02	102.78	124.84	231.12	171.92	0.34	ND

Mean values superscripted by the same letter are not significantly different within the column. Mean values of three measurements± standard deviation, NCS= native corn starch, A = native corn starch with ginger, B = native corn starch with garlic. CD = Critical Deviation, ND = not detected

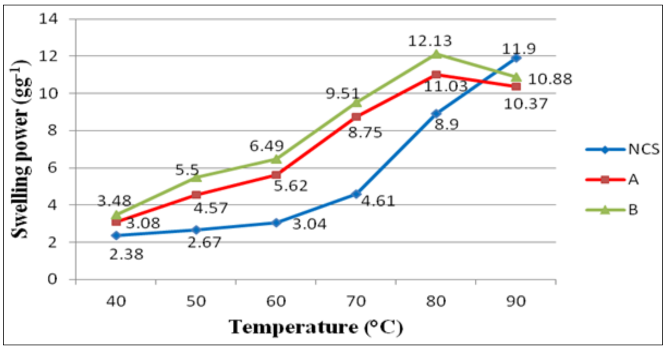

Fig 1: Swelling power native and cross-linked corn starches

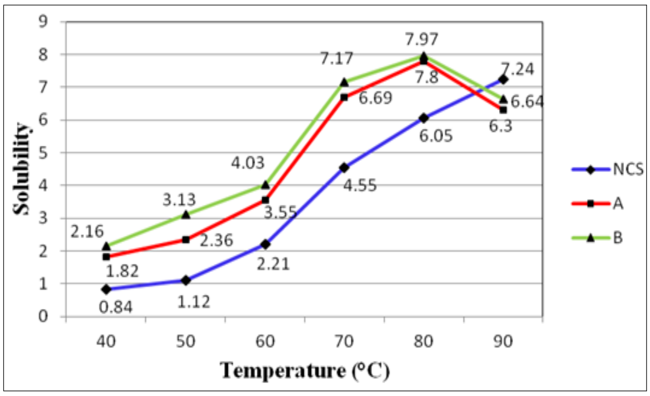

Fig 2: Solubility native and cross-linked corn starches

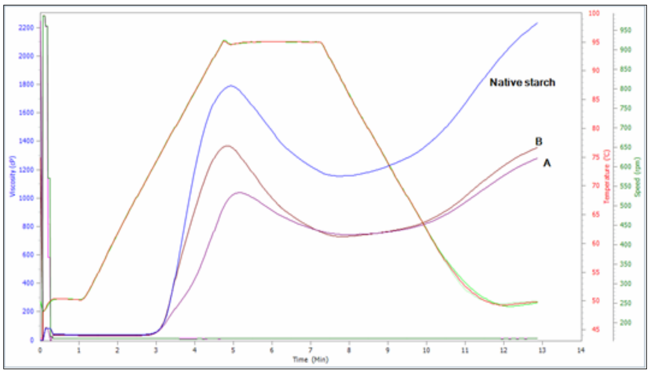

Fig 3: Pasting properties of the native and cross linked starches

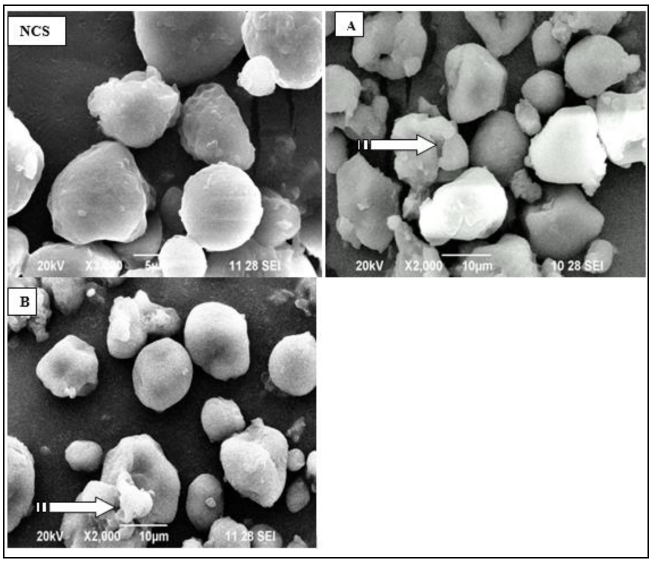

Fig 4: SEM Image of native and cross-linked corn starches

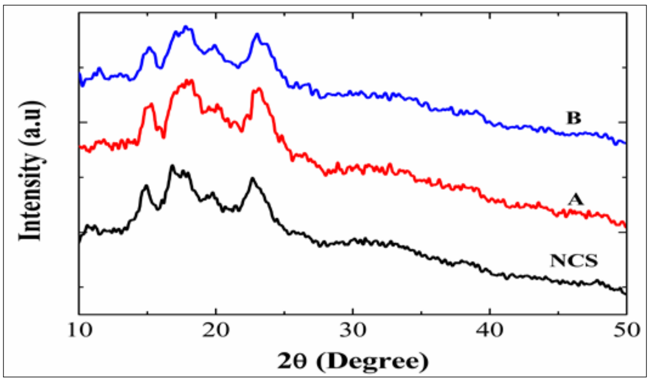

Fig 5: X-ray diffraction pattern of native and cross-linked cassava starches

Conclusion

Cross-linking agent influenced the physico-chemical, functional properties and viscosity characteristics of the corn starches to a considerable extent. Cross-linked starches had less protein, fat and moisture content than the native starch. These starches had higher ash and amylose content than the native corn starch. The swelling and solubility values were affected by the cross-linked reaction. The cross-linked starches exhibited lower peak viscosity, final viscosity, peak time and pasting temperature than their native counterpart. Cross-linked starches had compound granules and there granules were damaged. Therefore the study concluded that the cross-linking agents affected the structure of starch molecules within the granule, such as the distribution of the introduced cross-links.

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