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Physicochemical and Pasting Chracterization of Carboxymethylated Scarlet Runner Bean (*Phaseolus coccineus*) Starch

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ABSTRACT

Starch extracted from scarlet runner bean was subjected to carboxymethylation using sodium monochloroacetate in the presence of sodium hydroxide. Some physicochemical properties, proximate composition, and the pasting properties of the carboxymethylated scarlet runner bean starch (CM-SRBS) were compared with those of the native scarlet runner bean starch (NA-SRBS). Proximate composition studies show a significant rise in the moisture and ash content with a drop in the protein, fat, crude fiber and carbohydrate content in carboxymethylated scarlet runner bean starch compare to native scarlet runner bean starch. Physicochemical studies show higher water and oil absorption capacity for carboxymethylated scarlet runner bean starch, while the swelling property and solubility of the carboxymethylated scarlet runner bean starch is shown to be higher with relative increase with increase in temperature. The pasting properties of carboxymethylated scarlet runner bean starch compare to native scarlet runner bean starch are generally lower. These changes in the properties of native scarlet runner bean starch compared to its corresponding carboxymethylated scarlet runner bean starch can in many ways improve its industrial application and contribute to a sustainable development.

KEYWORDS: Scarlet runner bean, starch, carboxymethylation, proximate, physicochemical and pasting properties.

INTRODUCTION

Scarlet runner bean (*Phaseolus coccineus*) is a native of the central America mountains and broadly distributed in spain [1]. It belongs to the family leguminoseae, genus phaseolus and occupy the third position in the economic ranking among the different Phaseolus species [2]. It is planted mostly as an ornamental because of its rapid growth with abundance of large and brightly colored flowers, although the leaves, pods and the green shelled beans (i.e. immature) are edible in the fresh stage while the root is often eaten by Central America Indians [3,4], and has also been reported to be poisonous [5].

Scarlet runner bean contain high and pure starch [6] and carbohydrate content [7]. It is a less staple food in many countries including Nigeria and therefore, it can be cultivated to substitute for the conventional sources of starch (e.g corn, potatoes, and cassava) which are staple food.

Starch has found wide applications both industrially and domestically. Its regular occurrence, low cost and year round availability are its distinctions, while its major source is of high concentration in the main storage organs of plants which includes the seeds, fruits, stem , leaves, roots and tubers. The quest to obtain or synthesize novel starches especially for industrial applications has led to the extraction and modification of starches from different parts (i.e. storage organs) of different plants. Modification can affect starch solubility, viscosity, freeze-thaw stability, paste clarity and sheen, gel formation, film formation, cohesiveness, stability to acid, and retrogradation [8], in ways which will enhance the desired industrial applications.

Carboxymethylation of starch was first carried out in 1924 by Chowdury and it is a versatile functionalization procedure, as it provides access to biomaterials with valuable properties [9]. It can be generally described as the activation of the polysaccharide with an alkali hydroxide (e.g. NaOH) followed by its modification using monochloroacetic acid or its sodium salt according to Williamson ethers synthesis [10]. In this reaction, carboxymethyl group(s) is substituted for one or all the three (i.e. C2, C3, and C6) hydroxyl group(s) on each anhydroglucose unit (AGU) in the polysaccharide and the average number of substituted carboxymethyl group is referred to as the degree of substitution (DS), with values between zero and three [11]. Carboxymethylated starch (CMS) has been of wide application in the industries, replacing the native starch based on its more unique and

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improved properties which includes solubility, emulsification, suspension and water holding capacities [12]. Added to these properties are its relatively low viscosity and a reduction in retrogradation.

Hydrophilicity and solution clarity is also enhanced in the native starch by the introduction of the carboxymethyl group, and hence its improved solubility in aqueous systems [13]. The increase in hydrophilicity due to the reduced interparticle surface interaction resulting from an increase in repulsions on carboxymethylation of surface particles prevents interparticle agglomeration and thus enhances suspension stability [14]. Carboxymethylated starches are also non-Newtonian, i.e., the viscosity of their solutions will be Newtonian at low shear rate but will decrease at a critical shear rate [10]. These added properties which has improved the contributions of starch to the texture, viscosity, solubility, homogeneity, and moisture content of food products, plus the fact that no known carcinogenic effect or medical aggravations (other than a laxative effect if a large amount about ca. 10g is orally ingested) is caused due to the carboxymethylated starch [10], has settled the application of CMS in the food industry.

In the pharmaceutical industry, carboxymethylated starch is used as disintegrant in tablets and it has also been reported that CMS is preferably used as osmotic agents for adjusting the toxicity of drugs especially medicinal solutions for parenteral administration based on the swelling and solubility properties, and hence, its use in the treatment of dialysis [15].

Biodegradable beads have been produced from CMS crosslinked with ferric salt [10], while acrylonitrile grafted copolymer of crosslinked CMS has also been reported to be capable of effective removal of heavy metals ions from water [16]. And hence, its use in bioremediation of waste water. The properties and applications stated above for CMS are just among many that has been reported.

The production of legume protein can be of economic value only if the starch component is made profitable simultaneously [17]. Emphasis has also been laid on the need to harness the potentials of underutilized legumes as invaluable sources of starch [18,19].Therefore, the objective of this work is to modify the starch extracted from scarlet runner bean starch via carboxymethylation, study the proximate composition, physicochemical and pasting properties and compare these with those of the NA-SRBS for possible industrial application(s) recommendation.

MATERIALS AND METHODS

Materials

Dried Scarlet runner bean seeds were purchased in Ado-Ekiti central market, Ekiti State Nigeria, sodium hydroxide (NaOH), sodium monochloroacetate (NaMCA), hydrochloric acid, and sulfuric acid were obtained from Germany (Scharlau Chime S.A.) and ethanol was obtained from England (BDH chemical limited) and all materials were used without further processing or purification.

Sample Preparation

The seeds/beans were separated by removing the bad and defective ones manually and the good beans were kept in a knitted polyethylene bag in a cool dry environment with no further processing or extractions prior to analysis.

Isolation of Starch

Weighed (1Kg) quantity of the clean beans was soaked overnight in 4 liters of 0.5% NaOH aqueous solution after which the beans were dehulled manually. The dehulled beans were wet milled in a warring blender at low speed with ice cold 1% NaOH aqueous solution. The slurry obtained was suspended in 5 liters of distilled water and the pH was adjusted to 8.0 by adding 0.1M NaOH solution while stirring. The mixture was centrifuged, the cake was re-slurried in water and the slurry was screened using a 75μm screen to remove fiber. The starch obtained was washed twice with distilled water, dried at room temperature and labelled NA-SRBS.

Preparation of carboxymethyl Starch

Carboxymethylation was carried out using the method described by Stojanovic et al. [20]. 40g of NA-SRBS was added to 120ml ethanol and 28 ml aqueous 11.5M NaOH. The mixture was stirred for 20 minutes at 25°C and 28g sodium monochloroacetate (Na-MCA) was added. The reaction mixture temperature was raised and kept constant at 58°C with continuous stirring for 100 minutes (degree of substitution (DS) was assumed to range between 0.5-1.0 based on the amount of Na-MCA added). The synthesized sodium carboxymethylated starch (Na-CMS) was purified by dissolving it in water and the solution obtained was neutralized using 0.1M HCl solution. It was finally precipitated out using ethanol, filtered, dried under vacuum at 50°C, grounded and labeled CM-SRBS.

Proximate Composition Analysis

Samples (i.e. Na-SRBS and CM-SRBS) were analyzed for moisture content using method 950.46, crude fat using petroleum ether as the solvent extractor in a soxhlet apparatus as described by method 948.16, crude protein using Kjeldahl method also as described by method 984.13 in which the percentage nitrogen obtained was multiplied by 6.25 (i.e. the conversion factor) to convert it to percentage crude protein, crude fiber was determined using method 962.09, ash content was analyzed using method 942.05 [21]. Carbohydrate was obtained by difference 100% - %(moisture + protein + fat + crude fat + ash).

Physicochemical Properties

The water and oil absorption capacity (WAC and OAC) of the samples were determined using the method reported by Sathe and Salunkhe [22]. 1g of sample was mixed with 10ml distill water or oil (Executive chef oil, lever brothers PLC, Nigeria) in a vari-whirl mixer for 30 seconds. The mixture was allowed to stand for 30minutes at room temperature of 25-30ºC, after which it was subjected to centrifugation at 5000rpm for 30minutes. The volume of the supernatant was thereafter noted in a 10ml graduated cylinder, density of distill water assumed to be 1g/ml and that of oil was determined (0.87g/ml).

The effect of temperature on swelling and solubility in water was determined using the method by Adebowale et al. [18]. Accurately weighed (1g) sample was carefully placed in a clean test tube and weighed (W1). The starch was then dispersed in 50ml of distill water using a vari-whirl mixer. The resultant slurry was heated at 45, 55, 65, 75, and 85˚C respectively for 30minutes using water bath at regulated temperature. The mixture was thereafter cooled (30±2˚C) and subjected to centrifugation at 500 rpm for 15min. Aliquots (5ml) of the supernatants obtained after centrifugation was dried to a constant weight at 110°C and the residue obtained was designated to be the amount solubilized in water. Solubility was calculated in gram per 100 gram of starch on dry weight basis.

$$\%\text{solubility} = \frac{\text{weight of residue from supernatant}}{\text{weight of sample}} \times 100$$

The residue (i.e. sediment obtained after removal of the supernatant) was quantitatively transferred back to the cleaned, dried test tube and re-weighed (W2), and %swelling of water was calculated thus;

$$\%\text{swelling of starch} = \frac{W2 - W1}{\text{weight of starch}} \times 100$$

Pasting Properties

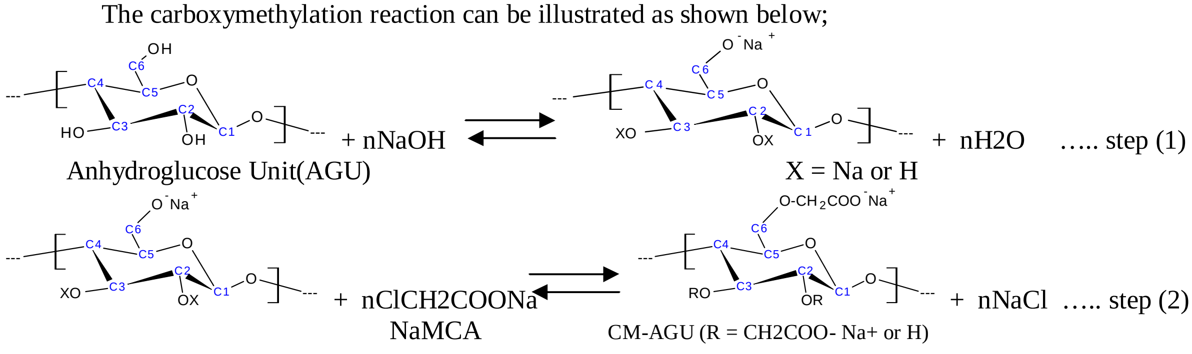
The pasting properties of the samples were evaluated using the rapid visco analyzer (RVA series 4, Newport Scientific, Sydney, Australia) on 10% starch slurry obtained while 2.8g of sample was suspended in distilled water and adjusted to a total weight of 28g in a canister inserted into the RVA machine. The sample was then equilibrated at 50°C for 1min, and further heated for 7.5min at 7°C/min. It was held at 95˚C for 5min and the cooled to 50˚C in 7.5min at 5.7˚C/min. The results (which are averages of triplicate determinations) obtained/calculated from the pasting curve includes; the initial pasting temperature, peak viscosity on heating, peak time, cold or final viscosity, trough (i.e. viscosity after holding at 95˚C for 30min), viscosity breakdown/breakdown (peak viscosity - trough), and the setback value (final/cold viscosity - trough).

Statistical Analysis

Data were obtained as mean of triplicate determinations and analysed by analysis of variance (ANOVA) method based on the General Linear Model (GLM), while significant differences were obtained on an ASA (User's guide version 6) package [23].

RESULTS AND DISCUSSION

The carboxymethylation reaction can be illustrated as shown below;



Step (1) & (2) are the activation and modification step respectively. "n" in the reaction above is in the range 1 ≤n≤3 and DS ranges from zero (i.e. when averagely, there is no substitution of carboxymethyl group) to three (i.e. when averagely, there is a complete substitution per AGU), and the susceptibility of the carbon atoms to substitution per AGU has been reported to decrease as follows, C2>C6>C3[24]. DS in a particular reaction medium (organic or inorganic) depends on the amount of NaOH, NaMCA, water content, reaction temperature, and time [25]. NaMCA can also react with NaOH to form sodium glycolate (as given below) in a side reaction that will affect the DS of carboxymethylation reactions [9,20].

NaOH + NaCl ⟶ OH—CH2COONa + NaCl

Based on the conditions employed, DS in this work is assumed to range between 0.5 - 1.0 [9,20]. And it has been reported that the DS of commercially available carboxymethyl cellulose typically related in properties and applications to CMS, ranges between 0.5 and 1.5 [26].

Proximate Composition Analysis

The results of the proximate composition analysis of the Na-SRBS and the CM-SRBS are presented on **Figure 1**. The results obtained for the ash content, crude protein and fat are all below 1%. This result establishes high level of purity of the starch samples [27] and the efficiency of the isolation method used.

The significant rise in the moisture content of NA-SRBS compare to CM-SRBS (6.97% and 13.29% respectively) may be due to the interruption of the ordered structure in the NA-SRBS on carboxymethylation, leaving more spaces for water molecules. Carboxymethylation generally increases hydrophilicity [14], hence the ability of CM-SRBS to retain more water at ambient temperature. Hydrophilicity also enhances effectiveness in processing, storage and uptake of food in particulate form by preventing agglomeration.

Crude protein, fat, crude fiber and carbohydrate are low in CM-SRBS (0.87% , 0.97%, 0.40 and 91.19) compare to NA-SRBS (0.14%, 0.32%, 0.83 and 85.00) respectively. The replacement of hydrogen atom(s) with carboxymethyl group(s) reduce carbohydrate functionality, this also minimized hydrogen bonding which reduce the starch interaction with other constituents such protein, fat and crude fiber leading to their easy removal during processes such filtration and washing of the CM-SRBS. The residual protein and/or lipid in the native starch can influence its flavor [8,27], therefore, CM-SRBS can be preferably used in industrial applications where such flavor may not be required e.g. textile, pharmaceutical, oil drilling mud, adhesives, etc

Higher ash content is obtained in CM-SRBS (0.42%) compared to the NA-SRBS (0.28%). This may be due to the introduction of mineral substances on modification (e.g. Na), which in appropriate amount can enhance the essential mineral in food, and can also inhibit the activities of microorganisms ($P \leq 0.05$).

The results obtained for the NA-SRBS can be favourable compared with those reported for sorghum CSH 9 starch by Ganorkar and Kulkarni [28], but on the contrary (except for protein content), the effect of carboxymethylation on the proximate composition is different.

Table1; Proximate Composition of CM-SRBS and NA-SRBS

	%Moisture Content	%Protein	%Fat	%Crude Fiber	%Ash	%Carbohydrate
NA-SRBS	6.97±0.12	0.87±0.02	0.92±0.03	0.40±0.01	0.28±0.02	91.19±0.95
CM-SRBS	13.29±0.20	0.14±0.01	0.32±0.01	0.83±0.04	0.42±0.02	85.00±0.94

Values within columns are significantly different ($P \leq 0.05$)

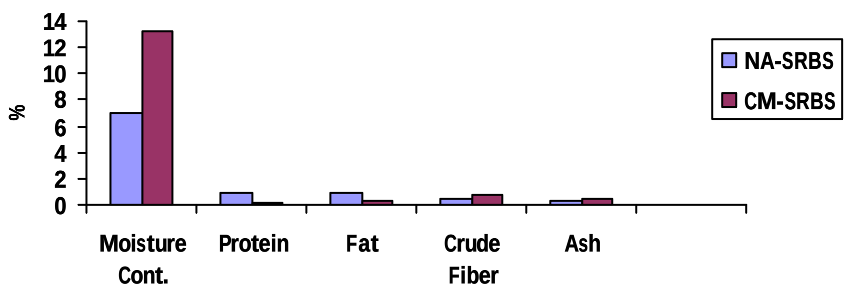


Figure1; Proximate Composition of NA-SRBS and CM-SRBS

Physicochemical Properties

As presented on **Table 2,** water and oil absorption capacities (WAC and OAC) are higher in CM-SRBS (713.8% and 87.89% respectively) compared to the NA-SRBS (122.92% and 65.6% respectively), and the elevation in WAC is relatively more. High WAC is due to the high affinity of the sodium carboxymethyl group for water molecules [29], and the interruption of the ordered structure in the NA-SRBS by the introduction of the bulky sodium carboxymethyl group, which leaves more spaces to be occupied by water molecules. These enhance hydrophilicity and improve both solubility and suspension stability [14]. Imbibition of water is an important functional trait in foods such as sousages, custards, and doughs [30]. The high WAC of the CM-SRBS can also recommend its application in bioremediation of waste water on further modification such as; conversion to water insoluble free carboxylic acid of the polymer by treating it with mineral acid [10,20], crosslinking and copolymerization [16].

The elevated OAC in the CM-SRBS can be attributed to an increase in physical entrapment of oil by capillary attraction [31]. The reasonable OAC obtained for CM-SRBS, which will induce hydrophobicity can be used to control the its water absorption. OAC is useful in structure interactions in foods, especially in flavor retention, palatability improvement, and extension of shelf life especially in bakery and meat products [32].

The solubility and swelling properties of the NA-SRBS and CM-SRBS at different temperatures are presented on **Table and Figure (3a) and (3b)**, and the data obtained for NA-SRBS can be favorably compared to those reported as the average values for some red beans by Han et al. [33]**.** The solubility and swelling properties of NA-SRBS increases on carboxymethylation with a correspondingly increase with increase in temperature, and this concur to the findings by Bhattacharyya et al. [34] and Nattapulwat et al. [11]. The low solubility of NA-SRBS which increases with increase in temperature is characteristic of that reported for legume starches [27,32,35]. The introduced sodium carboxymethyl group will enhance dissociation and hydrophilicity, hence higher solubility, dispersability in aqueous suspension by minimizing interparticle agglomeration [14] and exhibition of a polyelectrolyte behavior [10]. Higher solubility may also be due to the destruction of the crystallinity in the native starch [9]. One of the most important goals of carboxymethylation of cellulose and starch is to obtain water-soluble derivatives, which are applied in various fields in order to control the behavior of aqueous systems and preparations [10].

It has been reported by Madeneni et al. [36] that swelling is due to the acquisition of thermal energy by starch granules dispersed in water. The resulting thermal agitations weakens the intragranular bonds, which are proportional to the strength of the binding forces (majorly hydrogen bonding in NA-SRBS) and this increase with increase in temperature. Weaker binding forces (enhanced in this case by replacing hydrogen with the carboxymethyl group) relax more easily, causing the granule to absorb water and swell. Lower molecular weight amylose also got solubilized and leach out, this reduce the amylose content of the CM-SRBS which has been reported by Tester et al., [37] to inhibit swelling. The higher swelling in CM-SRBS could also be attributed to the low fat and protein (**Table 1**) which are important factors controlling the swelling [38]. Swelling and solubility are important properties of CMS used in the food industries, and also in pharmaceutical industries especially as osmotic agent for controlling drug toxicity and treating dialysis [15].

Table 2: Water and Oil Absorption Capacities of NA-SRBS and CM-SRBS

	WAC (%)	**OAC (%)**
NA-SRBS	122.92±0.97	65.6±0.88
CM-SRBS	713.82±0.95	87.89±0.96

Values within columns are significantly different (P≤0.05)

Table 3a: Swelling Properties of NA-SRBS and CN-SRBS with Change in Temperature

Temperature	**45°C**	**55°C**	**65°C**	**75°C**	**85°C**
NA-SRBS (%)	2.17±0.05	2.19±0.09	2.29±0.12	3.93±0.10	11.19±0.19
CM-SRBS (%)	24.11±0.62	24.67±0.65	25.80±0.59	28.40±0.55	33.47±0.60

Values within columns are significantly different (P≤0.05)

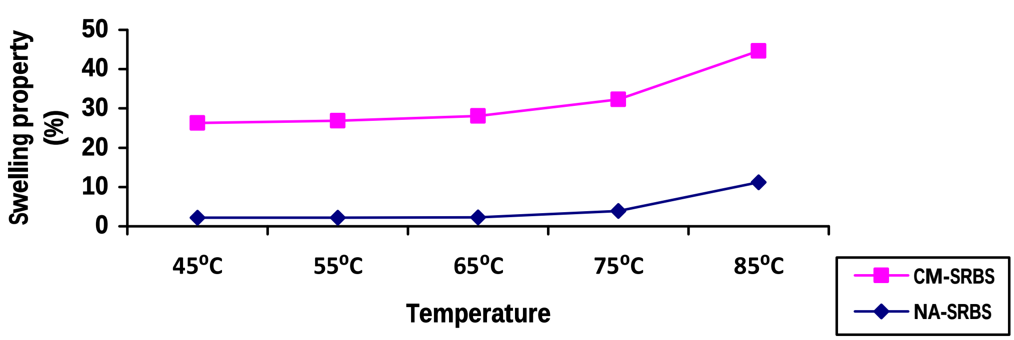


Figure 3a; Swelling Property of NA-SRBS and CM-SRBS with Change in Temperature

Table 3b: Solubility of NA-SRBS and CM-SRBS with Change in Temperature

Temperature	45°C	55°C	65°C	75°C	85°C
NA-SRBS (g/100g)	3.00±0.05	10.00±0.04	11.00±0.04	11.40±0.02	11.90±0.02
CM-SRBS (g/100g)	18.3±0.06	27.10±0.12	37.30±0.10	56.30±0.08	70.20±0.07

Values within columns are significantly different (P≤0.05)

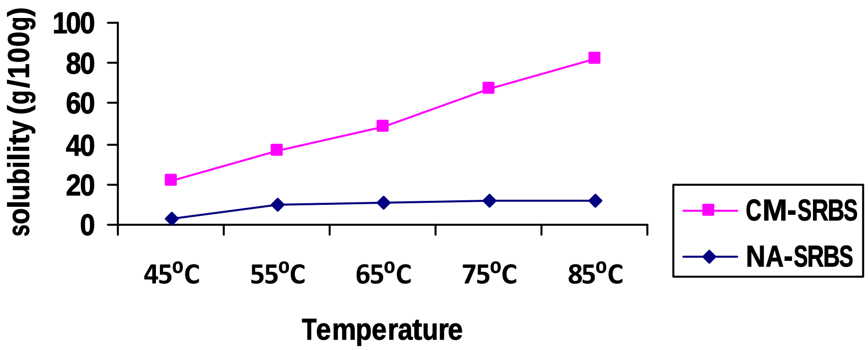


Figure 3b; Solubility of NA-SRBS and CM-SRBS wiyh Change in Temprature

Pasting Properties

When starches are dispersed in water and heated, it forms gel at a particular temperature with rise in viscosity, this is due to the change in the granular dimension and structure [27]. Some behavior and properties constitute this phenomenon and these are referred to as pasting properties/characteristics and this can differ from starches based on their sources, purity, and difference in chemical composition on modification. The pasting properties obtained from the pasting curve for CM-SRBS are compared with NA-SRBS on **Table (4).** Pasting started at 60.2°C for the NA-SRBS and this is within the range of average pasting temperature of some red beans reported by Han et al. [33], while CM-SRBS started pasting at 60.15°C. This lower but less significant change in temperature indicates granule fragility [24]. This will economizes the cooking energy and may also be utilized in products that are susceptible to high temperature [39].

The higher final/cold viscosity compared to the peak viscosity obtained for both NA-SRBS and CM-SRBS show that amylose leaches out of the swollen granule, so that the paste can be able to form a network on cooling [40].

The lower peak viscosity in CM-SRBS can also be due to a partial degradation in the structural network [27] and granule fragility, while the lower final/cold viscosity can be attributed to the restriction in the tendency of the molecules to realign after cooling, which will facilitate a lower setback [27], which is also obtained for the CM-SRBS compared to NA-SRBS. The setback is the index of retrogradation tendency of a starch paste [41], hence a lower retrogradation tendency for the CM-SRBS which indicate a potential for use in frozen foods [42]. More breakdown (i.e. change in viscosity when temperature was kept constant at 93ºC for 5min) obtained for CM-SRBS indicates a poor capacity of the starch paste to withstand sever processing conditions [36], and less resistance to heat compare to NA-SRBS. The trough (i.e. final viscosity after holding at 93ºC for 5mins)is also consequently lowered on carboxymethylation, while the lower pasting time obtained for CM-SRBS could be due to easy deformation of starch granules on modification, compared to the native starch. This will also economize cooking time.

The effects of carboxymethylation on the pasting properties of the NA-SRBS obtained in this work can be favourably compare to those reported by Olu-owolabi et al. [43], for acha (*Digitaria stapf*) grain.

Table 4: Pasting Properties of NA-SRBS and CM-SRBS

	NA-SRBS (RUV)	CM-SRBS (RUV)
Peak viscosity	361.58	193.17
Trough	263	112.83
Break down	98.58	80.34
Final viscosity	465.75	199.33
Set back	202.75	86.5
Peak time	4.37	2.09
Pasting temperature	60.2	60.15

CONCLUSION

Scarlet runner bean can be relatively consider as a less staple food, and also as a new and underutilized starch source in many parts of the world. For this reason, its use can be maximized by modifying its relatively high starch content via carboxymethylation which has been shown and analyzed in this work, while conserving the conventional sources of starch which includes; Yaw, Corn, Cassava, Potatoes and many others which are staple foods in this quest. The purity of the isolated starch is shown from the proximate analysis, while some industrially important properties of starch such as oil and water absorption capacity, swelling power, solubility and pasting properties are also shown to be enhanced while the results obtained are comparable and competitive with those from many reports. With the interpretations of these results, CM-SRBS can be recommended for industrial applications to contribute to a sustainable industrial development.

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