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CHARACTERISATION OF CITRATE STARCHES OF TWO VARIETIES OF LOCAL COWPEAS

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Abstract
Meeting industrial needs and native starch deficiencies requires exploring unconventional sources and starch modification, respectively. Local cowpeas, which are abundant and of restricted use to cultural practises, are a potential source of starch. In this work, starches were isolated from two local cowpeas - horse red and carton brown, and labelled Native Horse Red(NHR) and Native Carton Brown(NCB), respectively. They were modified using citric acid to produce the citrate derivatives, CHR and Citrate Carton Brown (CCB), respectively. The yields of NHR and NCB were 47.1 and 46.9 g/100 g, respectively. Selected physicochemical properties of native and modified starches were determined. The degrees of substitution of citric acid into native starches were not significantly ($p > 0.05$) different. CHR and CCB had significantly higher water and lower oil absorption capacities than their native counterparts. The modification improved the swelling powers and solubility of native starches with increased temperatures and pHs. Gelation properties of NHR were significantly improved by modification. Both starches had improved pasting properties. Light transmittance significantly reduced following starch modification and increase in starch storage period. The study showed that horse red and carton brown cowpea native starches and their citrate forms have potentials of being used in gelling, filling, flavour retention, and frozen foods.

Keywords: citric acid, cowpea, modification, properties, starch

INTRODUCTION

Native starch and its modification products are important in industrial applications because of their wide applications in food, paper, textile and pharmaceutical industries (Lawal, Adebowale, Ogunsanwo, Barba, & Ilo, 2005). However, in the unmodified form, starch use is restricted due to some undesirable properties it exhibits. These include being cold water insoluble, viscosity loss and reduced thickening power upon cooking, retrogradation, etc (Simsek, Ovando-Martínez, Whitney, & Bello-Pérez, 2012). These shortcomings of native starch, however, can be overcome by modification, which adds small ionic or hydrophobic functional groups to the molecules.

Chemical modifications of starch have attracted much attention. It has yielded starches with diverse applications in the food and non-food industries such as found in disintegrants, glidants, lubricants, fat replacers, thickeners, gelling agents, binding agents in paper, sizing agents and improvers of printing dyes in the textile industry (Tharanathan, 2005). Starch can be modified by cross-linking. This is commonly achieved using poly-carboxylic acids, epichlorohydrin, phosphoryl chloride ($POCl_3$), etc. Due to cross-linking, starch structure is stabilised and swelling is adjusted as desired in some food applications. Citric acid is considered as a non-toxic and inexpensive cross-linking agent, compared to many other cross-linking agents (Kim, Lee, & Chang, 2017). It produces citrate starch with improved freeze-thaw stability (Xie & Liu, 2004), resistant starch composition (Kim et al., 2017), reduced swelling power, gelling strength, solubility and retrogradation tendency (Martins, Gutkoski, & Martins, 2018).

The major sources of starch for food and non-food applications include maize, wheat, potato, yam, etc. These sources serve as staple foods for a large number of communities, especially, in developing countries. To avert the competition between the industry and table, there is a need to get starch from unconventional sources to ease the over-dependence on staple foods. Cowpea is an important crop in Africa because it is highly proteinous (Uwaegbute,

Iroegbu, & Eke, 2000), grows well on varieties of soil types and intercropping systems, is drought tolerant, and improves soil nutrient and prevents erosion. Its stems and leaves are economic gains as they serve as livestock feeds. Cowpea grain contains varying compositions such as 51 – 67% starch (Arora & Das, 1976), 11% moisture, 24% protein, 1.3% fat, 56.8% carbohydrate, 3.9% fibre, and 3.6% ash (Deshpande & Damodaran, 1990), 34.5 to 52% starch (Kerr, Ward, McWatters, & Resurreccion, 2000), and approximately 64% carbohydrate with starch being 33.3 g/100 g of the total carbohydrate (Ashogbon & Akintayo, 2013). The annual worldwide production of cowpea is more than 5.4 million tonnes of which Africa produces about 5.2 million and Nigeria accounting for 61% of Africa's production and by implication 58% worldwide (Hamid, Muzzafar, Wani, & Masoodi, 2015; Ojiako & Kayode, 2014). With the increasing need for starch as an industrial food raw material because of its functional properties, various sources and modifications have been attempted in the recent past. Literature however, is scarce on the modification of starches of local varieties of cowpea, such as carton brown and horse red. These cowpeas are abundant and cheap with restricted use to cultural practises. This justified the need for this work as a first attempt at unravelling the industrial potentials of the selected local cowpeas. This work was undertaken to isolate starches from two varieties of local cowpea, modify them by citrate cross-linking and determine the characteristic properties of the modified starches.

MATERIALS AND METHODS

Horse red and Carton brown cowpea seeds were purchased from the main market in Oja-Odan, Ogun State, Nigeria. The seeds were cleaned of foreign materials such as stalks and stones and damaged ones, separately milled into fine flours (Marlex Excella, KIL, Daman, India). The flours were defatted for 72 h by cold extraction using n-hexane and stored in a polythene bag until required. All chemicals used were of analytical grade apart from NaOCl, which was reagent grade.

Isolation of starch was carried out by the method of Lawal and Adebowale (2005) with modifications. 1 kg of defatted cowpea flour was suspended in distilled water at pH between 8.0 – 9.0. pH adjustment was done using 2 M NaOH solution at room temperature. It was stirred continuously for 4 h using a mixer (Kenwood, Kenwood Limited, Havant, Hampshire). The suspension was centrifuged at 4500 rpm (ROTANTA 460 R, Hettich GmbH & Co. KG, Tuttlingen, Germany) for 15 min. The residue obtained was suspended in distilled water (1:10) and screened using muslin cloth followed by centrifugation for 30 min at 4500 rpm. The starch pellet was washed twice with distilled water and dried for 48 h at 30 ± 2 °C in the oven (OV/125, Genlab Limited, Cheshire, England).

Citrate starch was prepared by the modified method of Xie and Liu (2004). Citric acid (100 g) was dissolved in 250 mL distilled water and the pH was adjusted to 3.5 with 10 M NaOH. The citric acid solution was mixed with 250 g starch and stored for 12 h in stainless steel tray at room temperature. The tray was then dried at 60 °C for 6 h. The mixture was ground and dried in a forced-air oven for 90 min at 130 °C. The dried mixture was washed severally to remove unreacted citric acid. The starch citrate was air-dried at room temperature, ground into fine powder and stored in labelled air-tight polythene bags until required. The starches were labelled, thus, native horse red starch, NHR; citrate horse red starch, Citrate Horse Red (CHR); native carton brown starch, NCB; citrate carton brown starch, CCB).

The degree of citrate substitution was determined by the method of Srikaeo, Hao, and Lerdluksamee (2019). Citrate starch (accurately 2.000 g) was weighed and 2 mL of distilled water and 50 mL of 1 M KOH solution were added. The whole sample was heated for 10 min in a boiling water bath. After cooling, the mixture was neutralised to pH 8.5 using 5 M acetic acid. Then, 25 mL of borate buffer (pH 8.5) and 0.3 g of an indicator (a mixture of murexide and Na_2SO_4 at a ratio of 1:500) were added. The volume was adjusted to 300 mL using distilled water and titrated with 0.05 M $CuSO_4$ until the red-violet colour disappeared. The degree of starch esterification with the acid was expressed as the quantity of citric acid residues in 100 g of preparation. The degree of substitution was calculated based on the average number of substituent groups per anhydroglucose unit (Eqn. 2.1).

$$DS = \frac{(162 \times W)}{(100 \times M) - (M - 1) \times W} \quad (2.1)$$

where W (% by weight of substituent) = [bound citrate (g)/sample (g) – bound citrate (g)] x 100, and M = molecular weight of the citric acid substituent which was 175.1. Native starch was used as control.

The method of Beuchat (1977) was used to determine water and oil absorption capacity of the starch.

Distilled water or oil (Power Oil, Nigeria) (10 mL) was added to 1 g of sample. The mixture was mixed thoroughly for 30 s and allowed to stand for 30 min. The volume of the supernatant was recorded. The mass of oil or water absorbed was expressed as g/100 g starch. Determinations of the effect of temperature on swelling power of starches were carried out in the temperature range of 55 – 95 ^{o}C, using the method reported by Lawal and Adebowale (2005) with modifications. 0.1 g of starch sample was 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 for 30 s. The resulting slurry was heated at desired temperatures, varied between 55 and 95 ^{o}C for 30 min using a temperature regulated water bath. The mixture was cooled to room temperature and centrifuged at 4500 rpm for 15 min. The residue after centrifugation with the water it retained and the test tube were weighed (W_2). Swelling power was calculated using Eqn. (2.2)

$$Swelling\ of\ Starch\left(g/100\,g\right)=\frac{W_2-W_1}{Weight\ of\ Starch}\times \quad (2.2)$$

The effect of pH on solubility and swelling was studied using the method of Lawal (2004). Slurry (1% w/v) was prepared with distilled water and the pH was adjusted to the desired value (2–10) with 0.1 M HCl or 0.1 M NaOH. The slurries were allowed to stand for 1 h, at 30±2 °C and centrifuged at 4500 rpm for 15 min. 5 mL of the supernatant was dried to constant weight at 110 °C to determine percentage solubility of the starch.

Gelation studies were done using the method of Lawal (2004). Samples of starch, 2–18% (w/v), were prepared in test tubes with 5 mL of distilled water. The starch suspensions were mixed for 5 min. The test tubes were heated for 30 min at 80 °C in a water bath, followed by rapid cooling under running cold tap water. The test tubes were further cooled at 4 °C for 2 h. Least gelation concentration was determined as that concentration when the sample from the inverted test tube did not fall down or slip.

Pasting properties of the cowpea starches were evaluated by using a Rapid Visco Analyzer (Newport scientific, RVA Super 3, Switzerland). The starch suspension (9%, w/w; dry starch basis, 10 g total weight) were equilibrated at 30 ^{oC} for 1 minute, heated at 95 ^{o}C for 5.5 min, at a rate of 6 ^{oC}/ min, held at 95 ^{o}C for 5.5 min, cooled down to 50 ^{o}C for 2 min. A programmed heating and cooling cycle was used. Parameter recorded were pasting temperature, peak viscosity, trough viscosity, final viscosity, peak time, breakdown viscosity and setback viscosity.

Light transmittance was studied using the method of Bhandari and Singhal (2002), with modifications. Starch (50 mg) was suspended in 5 mL of distilled water, using 10 mL cotton-plugged test tubes. The test tubes were then heated in a boiling water bath (with occasional shaking) for 30 min. After cooling to ambient temperature, the percentage transmittance (%) was determined at 650 nm against a water blank using a spectrophotometer (Jenway 6300 spectrophotometer). Also, to monitor tendency for retrogradation, samples were stored for 24 h at 4 °C to effect nucleation, after which they were stored at 30±2 °C for 1, 2, 4, and 6 days before determining the absorbance.

All analyses were done in triplicate. Means and standard deviations of triplicate determinations were calculated. Analysis of variance was performed to calculate significant differences in treatment means and least significant difference ($p < 0.05$) was used to separate means using SigmaPlot for Windows 14.0 (Systat Software, Inc.).

RESULTS AND DISCUSSION

The yields of native starches of horse red and carton brown cowpeas were 47.1 and 46.9 g/100g cowpea seeds, respectively. The starch yields were not significantly different ($p > 0.05$) and were similar to those reported by other workers (Kerr et al., 2000). Varying starch quantities have been reported for different types of cowpeas (Arora & Das, 1976; Ashogbon & Akintayo, 2013; Kerr et al., 2000). Variations in starch yields can be attributed to differences in botanical origin, purity attained and starch isolation methods.

The results of the degree of substitution of citric acid into CHR and CCB showed insignificantly different ($p > 0.05$) values of 0.12 and 0.14 g/100g starch. The DS obtained were similar to those reported for citric acid-modified starches of corn (Xie & Liu, 2004), cassava (Mei, Zhou, Jin, Xu, & Chen, 2015) and unripe plantain (Sanchez-Rivera, Nunez-Santiago, Bello-Perez, Agama-Acevedo, & Alvarez-Ramirez, 2017) done under similar experimental conditions. The DS is a function of the reaction conditions of temperature, time, starch origin (Xie & Liu, 2004), concentration of citric acid (Srikaeo et al., 2019) and pH (Lee, Lee, & Lee, 2018).

Water and oil absorption capacities of native and citrate cowpea starches (Figs. 1) revealed significant variations. No significant differences ($p < 0.05$) were observed in the water and oil absorption capacities of the native starches, NHR and NCB. Both CHR and CCB had significantly higher water and lower oil absorption capacities than their native counterparts. CHR, however, had better water and oil absorption capacities than CCB. For both cowpea samples, modification significantly improved the water absorption capacities of their native starches. Higher water absorption capacities of citrate modified starches over their native counterparts have similarly been reported for *Icacina* (Omojola, Orishadipe, Afolayan, & Adebiyi, 2012), yam cultivars (Falade & Ayetigbo, 2015) and sweet potato (Babu, Parimalavalli, & Rudra, 2015). Both cowpea starches had higher WAC than those reported for sweet potato (0.3621±1.17 – 0.5615±4.40 g/g) (Babu et al., 2015) and yam cultivar (0.803±0.006 – 1.047±0.023 g/g) (Falade & Ayetigbo, 2015) starches. The higher WAC of citrate starches can be as a result of increased hydrophilic tendencies caused by the introduced citrate functionality (Zehra, Mohsin Ali, & Hasnain, 2020). The variations observed in WAC among modified starches of cowpeas are attributed to differences in their botanical origins (Mweta et al., 2008). The decrease in oil absorption capacities following cross-linking of starches can be attributed to the increased hydrophilicity of the citrate starches. This implies that the native forms of carton brown and horse red local cowpeas can serve better as flavour retention agents and provide enhanced mouth feel where high oil contents are desired.

The results of the effects of temperature (55 – 95 ºC) and pH (2 – 12) on swelling power and solubility of the native and modified carton brown and horse red cowpea starches are shown in Figs. 2 – 5. Swelling power and solubility ranged from 0.41 g/g at 55 ºC – 2.20 g/g at 95 ºC and 1.50 g/g at 55 ºC – 14.5 g/g at 95 ºC, respectively. The range of values obtained was similar to those reported for plantain cultivars (Olatunde, Arogundade, & Orija, 2017) and Indian palo rhizome (Das, Jha, & Kumar, 2015) starches. An increase in swelling power and solubility with increase in temperature was observed. Similar observations of increase in swelling power with temperature were reported for hybrid maize (Lawal et al., 2005), jack fruit (Dutta, Kumar, Kalita, & Lata, 2011), *Icacina trichantha* (Omojola et al., 2012), lotus seed (Guo et al., 2015) and African breadfruit (Oderinde, Ibikunle, Bakre, & Babarinde, 2020) starches. NCB and CCB had better swelling powers and solubility than their horse red cowpea starch counterparts. In both cowpea starches, however, the modified forms had significantly higher ($p < 0.05$) swelling power and solubility than the native starches. While some workers have reported that modification improved swelling power and solubility of starches, others reported to the contrary. Improvement in swelling power and solubility following modification was reported by Zehra et al. (2020), Zieba, Kapelko, and Szumny (2013) and Ibikunle et al. (2019). Dutta et al. (2011), Sun et al. (2015), and Shaikh, Ali, Mustafa, and Hasnain (2019), on the other hand, reported a reduction in swelling power and solubility following the modification of starch. Observed swellings in modified starches are attributable to disorganization of birefringence due to increase in the perturbation caused by heating and then bulky functional group in the starch molecule with the resultant percolation of water (Lawal et al., 2005). The ability of modified starches to increase swelling power and solubility implies their suitability as tablet disintegrants and food digestibility improvers (Omojola et al., 2012).

The results of the effect of pH on the swelling power and solubility of cowpea starches (Figs. 4 and 5) showed variations in swelling power and solubility with pH. The increase in pH had a direct effect on both parameters increasing with pH increase. At all pH values examined, modified horse red and carton brown starches had

Fig. 1. Water and oil absorption capacities of native and citrate carton brown determinations

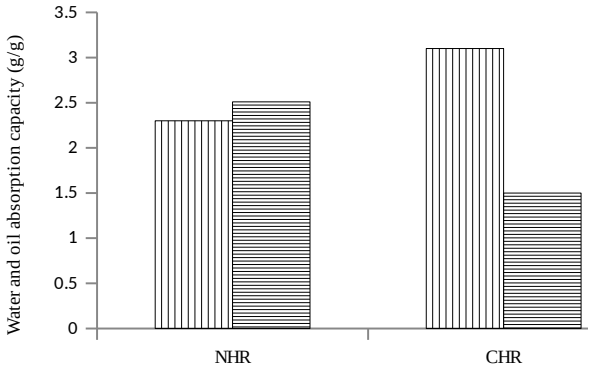


Fig. 2. Effect of temperature on swelling power of native and citrate carton brown determinations

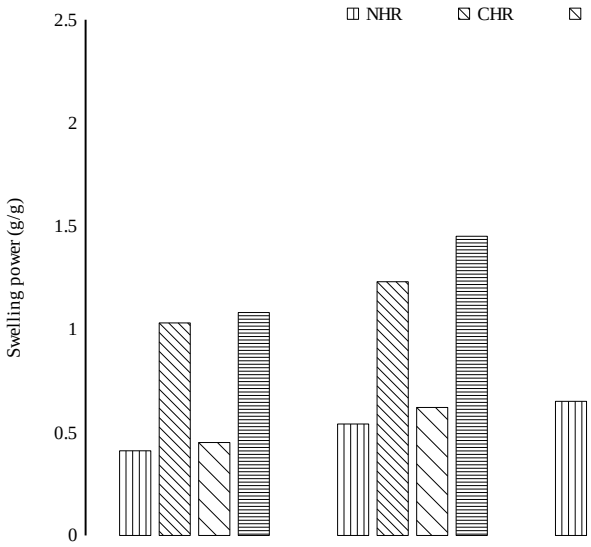
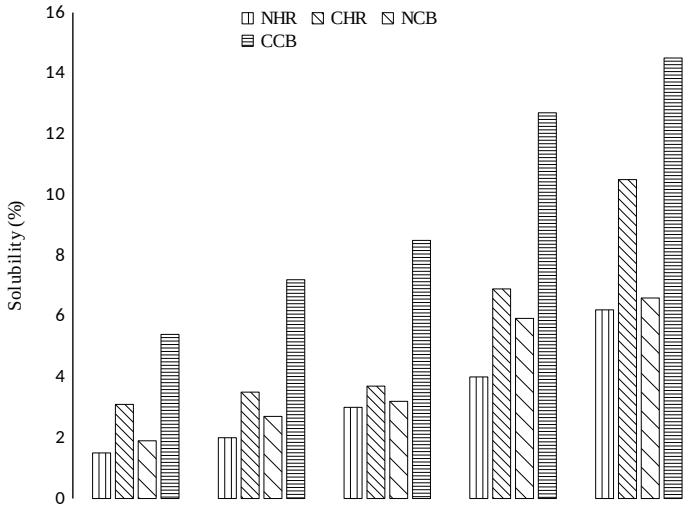


Fig. 3. Effect of temperature on solubility of native and citrate carton brown and horse red cowpea starches. Error bars are standard deviations of replicate determinations



significant increase in the swelling capacity and solubility compared with the native starches. CHR, however, had significantly higher ($p < 0.05$) swelling power and solubility than CCB. At the pH range of 2 – 6, NCB had higher swelling capacity compared to NHR while it was the reverse at 10 – 12 pH range. At pH 8, both native starches had the same swelling capacity (0.75 g/g). For native starch solubility, however, NCB had significantly higher values than NHR at the pHs except 8. Lawal et al. (2005) and Olayinka, Adebowale, and Olu-Owolabi (2013) reported higher swelling powers in native starches over modified starches and higher solubility of modified starches over the native counterpart. Higher swelling and solubility at the alkaline range pH could be attributed to increased hydrophilicity caused by the negative charges of starch and protein molecules (Adebowale, Afolabi, & Lawal, 2002; Olayinka et al., 2013) or partial gelatinisation of starch (Lawal, 2004). Industrial processing occurs in media with different pHs. Citrate horse red starch will therefore be suitable as fillers at higher pH values.

Fig. 5. Effect of pH on solubility of native and citrate carton brown
and horse red cowpea starches. Error bars are standard deviations of replicate dterminations

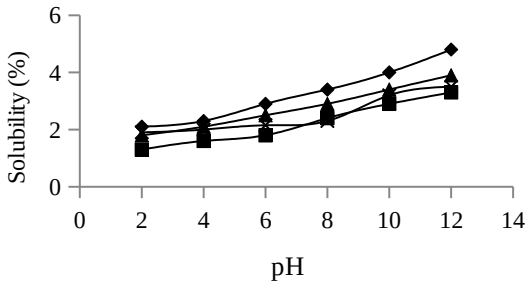
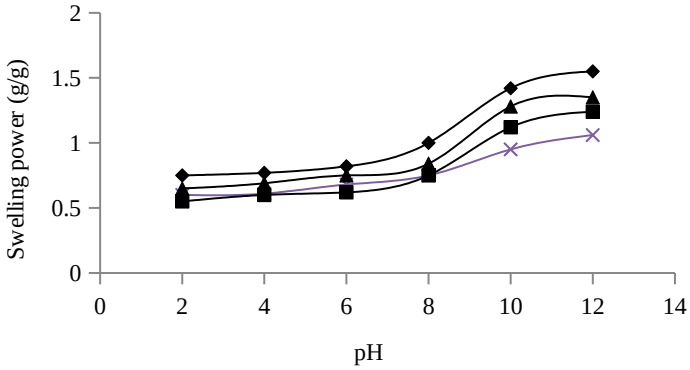


Fig. 4. Effect of pH on swelling power of native and citrate carton brown and horse red cowpea starches. Error bars are standard deviations of replicate determinations



The least gelation concentration (LGC), an index of network formation in starch gel, was measured as the minimum percent concentration of starch suspension in water forming a gel. The lower the value, the higher the ability of the starch to form a gel in water and as such use as a gelling agent (Kaur, Singh, & Singh, 2007). The tendency of starch samples to gel increased with increasing concentration of starch suspension (Table 1). The range of LGC obtained was 8 – 12% $^{w}/_{v}$. Among the starches, horse red cowpea starches had better gelling properties than their carton brown cowpea starch counterparts. Citrate modification resulted in a reduction of LGC of both cowpeas native starches. The ranking of the starches in order of decreasing gelling ability was CHR (8% w/v) > NHR (10 % w/v) > NCB = CCB (12 % $^{w}/_{v}$). The reduction in LGC following modification has been reported for acetylated bambara groundnut (Adebowale et al., 2002) and acetylated and oxidised water yam (Awolu & Olofinlae, 2016) starches. In contrast, an increase in LGC after modification of starch has been reported for jackfruit (Naknaen, Tobkaew, & Chaichaleom, 2017) and pigeon pea (Olagunju et al., 2019) starches. Gelation occurs as a result of structural transformation following gelatinisation, swelling and water imbibition to form rigid three-dimensional structures (Lawal & Adebowale, 2005).

Rapid visco-analyser pasting results of the citrate starches of horse red and carton brown cowpeas are presented in Table 2. The citrate starches of both cowpeas showed significantly low pasting properties compared to the native starches, with CHR having the lowest values. Reduction in peak viscosity after starch modification has been reported for starches from different unconventional sources (Astuti, Widaningrum, Asiah, Setyowati, & Fitriawati, 2018; Huo et al., 2018; Kim et al., 2017; Oderinde et al., 2020). The citrate starches had fragile surfaces due to surface erosion, caused by citric acid modification, before being subjected to pasting. They were thus weak under shearing and heating conditions. As they absorbed water, granules showed reduced extent of swelling and size, and so exhibited decreased peak viscosities (Huo et al., 2018). Contrary to reduced peak viscosity of starch upon modification, Awolu and Olofinlae (2016) reported increased peak viscosity of water yam starches after modification. The highest peak viscosity was exhibited by NCB. This reflected that NCB granules were the most ruptured during pasting of the starches (Ikegwu, Nwobasi, Odoh, & Oledinma, 2009). Breakdown and setback viscosities of the starched also showed trends similar to those of the peak viscosity in which there were high in the native starches but reduced by modification. The trend of mechanical/thermal stabilities and reduced retrogradation tendencies exhibited by the starches, implied by the breakdown and setback viscosities, respectively, was CHR > CCB > NCB > NHR. Increased mechanical and thermal stabilities are associated with reduced breakdown viscosity. The modification significantly increased the stability of the cowpea starches with CHR being the most stable. The reduction in breakdown viscosities of modified starches has also been reported by other workers (Astuti et al., 2018; Chan, Bhat, & Karim, 2009; Kaur & Singh, 2019; Raina, Singh, Bawa, & Saxena, 2007) and could be due to the strengthening of starch granule chains by citrate cross-linking (Astuti et al., 2018).

Table 1. Gelation properties of native and citrate carton brown and horse red cowpea starches.

Concentration (% $^{w}/_{v}$)	Starch sample			
	NHR	NCB	CHR	CCB
2	L	L	L	L
4	L	L	V	L
6	V	V	V	V
8	V	V	G	V
10	G	V	G	V
12	G	G	G	G
14	G	G	G	G
LGC[a]	10	12	8	12

CHR, Citrate Horse Red; NHR, Native Horse Red; CCB, Citrate Carton Brown; NCB, Native Carton Brown; LGC[a], Least Gelation Concentration.

The setback viscosities of the citrate starches were considerably lower than those of the native starches, which can be attributed to the stability conferred by citric acid crosslink. Reduced setback viscosities are associated with reduced tendencies of starch retrogradation (Babu et al., 2015; Shafie, Cheng, Lee, & Yiu, 2016; Yang et al., 2016). Lower setback viscosities have also been reported for acid-modified arrowroot (Astuti et al., 2018), rice (Huo et al., 2018; Kim et al., 2017) and sweet potato (Babu et al., 2015) starches. Different times and temperatures were required for the starches to cook. The orders of peak time and pasting temperatures were CCB > CHR > NHR > NCB and NCB > NHR > CCB > CHR, respectively. The modification significantly reduced the pasting temperatures of the native cowpea starches. The reductions are attributed to disrupted structural integrity caused by erosion of the granule surface, disorganised molecular order, and hydrolysis of the amorphous layer of starch. Structural compromise led to the promotion of water permeation into semi-crystalline structures (Huo et al., 2018). The pasting temperatures corroborate the swelling powers of the starches. Higher pasting temperatures indicate lower swelling capacities (Awolu & Olofinlae, 2016). Similar reductions in pasting temperatures of modified starches over the native counterparts abound in literature (Awolu & Olofinlae, 2016; Heebthong, Khanarak, Ruttarattanamongkol, & Khanitta, 2016). The results of the pasting properties imply that the citrate starches of the two cowpeas are potential additives in products requiring freezing, low viscosity and high water absorption.

The results of light transmittance of native and modified carton brown and horse red cowpea starches are presented in Table 3. Transmittance reduced following starch modification and with the increase in starch storage days from the 1st to 6th. NHR and NCB showed significantly ($p < 0.05$) higher transmittance values than their modified counterparts just as observed by Thys, Aires, Marczak, and Norena (2013) and Shaikh et al. (2019). This is due to the starch granules being strengthened by citrate cross-linking, thus reflecting the incident light rays rather than transmitting them (Liu et al., 2014). Alternatively, Lawal (2004), Dutta et al. (2011), and Mehboob, Ali, Alam, and Hasnain (2015), reported improved light transmittance following starch modification. Observations relating to reduction in transmittance (%) to increase in the length of the storage period have also been reported (Dutta et al., 2011; Lawal, 2005; Lawal, 2004; Moin, Ali, & Hasnain, 2017). Reduction in transmittance was however pronounced in the modified starches with CHR leading. This is attributable to the interactions of amylose and amylopectin initially leached during starch gelatinisation (Lawal, 2005). The implications are that native starches possess better aesthetic values when used as food additives in which the original colours of preparations are not to be clouded.

Table 2. Pasting characteristics of native and citrate (modified) starches of carton brown and horse

red cowpeas starches

Sample	Parameter						
	Peak Viscosity (cP)	Trough Viscosity (cP)	Breakdown Viscosity (cP)	Final Viscosity (cP)	Setback Viscosity (cP)	Peak Time (min)	Pasting Temperature (°C)
NHR	3491.00[a]	2441.00[a]	1050.00[a]	4304.00[a]	1863.00[a]	5.07[a]	80.80[a]
NCB	3669.00[a]	2716.00[b]	953.00[a]	4239.00[a]	1523.00[b]	5.00[a]	81.50[b]
CHR	-13.00[b]	-15.00[c]	2.00[b]	-6.00[b]	9.00[c]	5.63[b]	61.50[c]
CCB	19.00[c]	16.00[d]	3.00[b]	49.00[c]	33.00[d]	6.93[c]	63.00[d]

NHR: Native horse red; NCB: Native carton brown; CHR: Citrate horse red; CCB: Citrate carton brown. Values in the same column with different alphabets are significantly different.

Table 3. Influence of storage days on light transmittance of native and citrate carton brown and horse red starches

Starch Sample	Transmittance (%)			
	1st Day	2nd Day	4th Day	6th Day
NHR	1.93±0.41[aA]	1.57±0.17[aA]	1.45±0.15[aA]	1.40±0.13[aA]
CHR	1.01±0.16[bB]	0.88±0.13[bB]	0.65±0.06[bB]	0.40±0.08[bB]
NCB	1.96±0.08[aA]	1.60±0.08[aA]	1.35±0.13[aA]	1.30±0.06[aA]
CCB	0.88±0.08[bB]	0.71±0.10[bB]	0.55±0.13[bB]	0.55±0.06[bB]

Values are means ± standard deviation. Means in each row and column followed by different superscripts are significantly different at $P < 0.050$; capital (A, B) and small (a, b) show statistical differences for data in rows and columns, respectively.

CONCLUSION

Starches were isolated from horse red and carton brown cowpeas and modified using citric acid. Characteristics of the native and citrate derivatives of local cowpeas starches were investigated with a view to understand their possible uses as industrial raw materials. The modified cowpea starches had better water absorption capacities and can serve in thickening and filling. The native starches with better oil absorption are potential flavour retention agents. The ability of the modified starches to increase in swelling power at increased temperatures makes them suitable as tablet disintegrants and food digestibility improvers. The modification improved the pasting properties of native cowpea starches and increased their potentials as additives in products requiring freezing, low viscosities and high water absorption. The effects of modification of starches on starch crystallinity should be established using X-ray diffraction

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