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Research Paper

Morphological and functional properties of starches from cereal and legume: A comparative study

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Abstract. The isolation, composition, morphology and functional properties of rice (*Oryza glaberrima*) starches (ILRS, Ilaje rice starch; IGRS, Igbemo rice starch) and cowpea (*Vigna unguiculata*) starches (WCS, white cowpea starch; BCS, brown cowpea starch) from different cultivars were studied and compared. Rice starches were isolated from their flours by using a modified deproteination method in 0.1% NaOH. In contrast, the cowpea starches were isolated from their grains by using distilled water. The highest starch yield of 48.40% was obtained from Ilaje rice with a residual protein of 0.43% and the lowest starch yield of 38.00% from brown cowpea grain with a residual protein of 0.07%. The protein, fats and ash contents of the rice starches were slightly higher than those of the cowpea starches. SEM showed that rice starch granule shape was irregular, polygonal and angular-shaped, in contrast the cowpea starch granules were bigger and their shapes varied from round to ellipsoid. The formation of compound granules was only found in the rice starches. The dispersibility of the rice starches was higher than those of the cowpea starches and the reverse was the case in bulk density. When heated from 55 to 95°C at 10°C intervals, starches with higher amylopectin content had higher swelling power. The pasting parameters of the starches were significantly different.

Keywords: Rice starches, cowpea starches, pasting properties, dispersibility.

INTRODUCTION

Starches from different botanical sources are unique in their chemical compositions, morphologies and functionalities. This is to be expected due to differences in amylose (AM)/amylopectin (AP) ratio, genotype, soil type (during growth) and intensity of radiation of the sun during growth. Generally, for example, the legume starches are known for their high amylose content and consequent tendency to undergo retrogradation and syneresis, these idiosyncrasies tend to limit their applications in the food industry. In contrast, cereal starches possess lower AM content and smaller granules. The latter property ensures their applications in the cosmetic industry (especially in powder making). Additionally, the whiteness, bland flavor, easy digestibility, hypoallergenicity associated with rice (*Oryza glaberrima*) starches stand it out when compared to other cereal and non-cereal starches (Ashogbon and Akintayo, 2012a).

The isolation of starch from rice flour is bedeviled with protein associated with starch in rice endosperm and small granules of rice starch are slow to settle in aqueous medium, thereby constituting losses during separation and purification. In contrast, difficulties in the isolation of starches from legume (e.g. cowpea, *Vigna unguiculata*) have been attributed to the presence of a highly hydrated fine fiber fraction (Vose, 1977) which is derived from the cell wall enclosing the starch granules (Schoch and Maywald, 1968).

The individuality of starches is best seen in the differences in the morphology of their granules. The

Figure 1. White cowpea seeds.

morphology of starch granules depends on the biochemistry of the chloroplast or amyloplast, as well as the physiology of the plant (Bodenhuizen, 1969). Rice (*Oryza sativa*) starch granules are very small (Dang and Copeland, 2004) ranging from 3 to 10 µm (Bechtel and Pomeranz, 1978) with a unimodal distribution. They are polygonal and angular-shaped. By contrast, legume starch granules like that of cowpea is generally bigger and variable, ranging between 4 and 80 µm (Hoover and Sosulski, 1991). Legume starch granules may be oval, spherical, elliptical, or irregular depending on the biological source.

Pasting encompasses the changes that occur after gelatinization upon further heating and these include further swelling of granules, leaching of molecular components from the granules and eventual disruption of granules especially with the application of shear forces (Tester and Morrison, 1990). The effect of amylose (AM) and amylopectin (AP) on the pasting properties of rice starch has been widely reported (Li et al., 2008). Atuobi et al. (2011) studied starches from four cowpea cultivars and concluded that there are differences in their pasting properties, indicating discrepancies in cooking time. According to Henshaw and Adebowale (2004), swelling power (SP) increased progressively with increasing temperature for all starches of cowpea cultivars evaluated by them.

So much has been written on Nigerian rice flour (Otegbayo et al., 2001; Oko and Ugwu, 2011) but there is paucity of work in the literature on Nigerian rice starch. The few works on rice starch from Nigerian rice cultivars are due to Lawal et al. (2011) and Ashogbon and Akintayo (2012a, 2012b). On the other hand, literature review reveals plenty of information on cowpea flours (Kerr et al., 2000; Henshaw et al., 2002). But there is limited information in the literature on cowpea starches especially in the areas of pasting, dispersibility, pH and bulk density. Therefore, the objective of this work was to investigate and compare the functional and morphological properties of starches of two cultivars of rice (cereal) and two cultivars of cowpea (legume).

MATERIALS AND METHODS

Materials

White cowpea seeds (Figure 1) and brown cowpea seeds

Figure 2. Brown cowpea seeds.

(Figure 2) were purchased from the local market in Akungba, Ondo State, Nigeria. Dried rough rice (*Oryza glaberrima*) samples given local names of Igbemo rice (IGR) and Ilaje rice (ILR) were purchased from farmers. Igbemo is located in Ekiti State and Ilaje is in the riverine area of Ondo state, all in Nigeria. IGR is upland rice and Ilaje is lowland rice. All the chemicals used in the different studies were of analytical grade.

Isolation of starches

Rice starch was isolated from rice flour by using the alkaline deproteination method of Lim et al. (1999) as modified by Ashogbon and Akintayo (2012a). Briefly, rice grain was first dehulled and ground to powder using a laboratory grinder. Rice flour (200 g pass through 1 mm sieve screen) was mixed with 500 ml of 0.1% NaOH. The mixture was stirred on a magnetic stirrer for 3 h, and stored at 4°C overnight. The supernatant was decanted, and fresh volume of sodium hydroxide was added to the solid phase and stirred for another 3 h at ambient temperature. The procedure was repeated twice after which the solid phase was washed with 0.1% NaOH, blended and filtered. Distilled water was added to the filtrate and allowed to stand for 3 h. The supernatant was decanted and distilled water was added again. The procedure was repeated several times until the pH of the filtrate was between 6.0 and 6.5. The starch residue was collected and dried in a vacuum oven (N505F, YOGOII, GenlabWidnes, England) at 40°C for 48 h.

400 g of cowpea seeds were steeped in distilled water for 2 h. The seed coats were manually removed and the inner endosperm blended for 5 min at slow rotation using a laboratory blender. The slurry was diluted with distilled water and allowed to stand for 1 h. The supernatant was decanted and distilled water added to the starch residue. Repeated dilution and decantation continues until the pH is neutral. The prime starch residue was collected and dried in a vacuum oven (N505F, YOGOII, Genlab Widnes, England) at 40°C for 48 h.

Gross chemical compositions of isolated starches

Apparent amylose (AAM) content (%) was determined by colorimetric iodine assay index method, according to Juliano (1985). The moisture, protein, lipid, and ash content in the starch samples were determined using procedure of AACC method (2000).

Morphology of starch granules

The morphology of the starch granules was evaluated by

Table 1. Yield, chemical composition and AAM concentration of starches from cereal and legume.

Cultivars	Yield (%)	Moisture (%)	Protein (%)	Fats (%)	Ash (%)	*AAM (%)
ILRS	48.40 ± 0.12^{a}	12.77 ± 0.03^{a}	0.43 ± 0.01^{a}	0.50 ± 0.1^{a}	0.23 ± 0.01^{a}	22.64 ± 0.01^{a}
IGRS	45.70 ± 0.1^{b}	10.90 ± 0.01^{b}	0.42 ± 0.01^{a}	0.10 ± 0.01^{b}	0.20 ± 0.01^{a}	21.88 ± 0.01^{b}
WCS	40.00 ± 1.1^{c}	11.54 ± 0.03^{c}	0.09 ± 0.01^{b}	0.05 ± 0.00^{b}	0.03 ± 0.01^{b}	27.06 ± 0.03^{c}
BCS	38.00 ± 1.9^{d}	10.18 ± 0.42^{d}	0.07 ± 0.01^{b}	0.07 ± 0.01^{b}	0.05 ± 0.01^{b}	29.53 ± 0.05^{d}

Uncommon superscripts along columns indicate statistically significant difference ($P < 0.05$). *Apparent amylose (AAM)

scanning electron microscope (SEM) (QUANTA FEG 250 ESEM). Starch samples were suspended in 95% ethanol and mounted on circular aluminum stubs with double-sided sticky tape. The starch granules were evenly distributed on the surface of the tape, and the ethanol was allowed to evaporate. The samples were then coated with 12 nm gold, examined and photographed at an accelerating voltage of 10 kV with a magnification of X1000, X2000 and X4000.

Swelling power and solubility

Swelling power (SP) and water solubility index (WSI) determinations were carried out in the temperature range of 55 to 95°C at 10°C intervals using the method of Leach et al. (1959) and Holm et al. (1985), respectively.

Bulk density

This was determined by the method of Wang and Kinsella (1976) with slight modification. In brief, 10 ml capacity graduated cylinder was filled with the starch powdery sample. This was done by gently tapping the bottom of the cylinder on the laboratory bench several times until there is no further diminution of the sample level after filling to the 10 ml mark.

$$\text{Bulk density (g/ml)} = \frac{\text{Weight of sample (g)}}{\text{Volume of sample (ml)}}$$

Dispersibility

This was determined by the method described by Kulkarni et al. (1991) as recently modified by Akanbi et al. (2009).

pH

Starch samples (5 g) were weighed in triplicate into a beaker, mixed with 20 ml of distilled water. The resulting suspension stirred for 5 min and left to settle for 10 min. The pH of the water phase was measured using a calibrated pH meter (Benesi, 2005).

Pasting properties of starches

The pasting properties of the starches were evaluated by using a Rapid Visco Analyzer (Newport Scientific, RVA Super 3,Switzerland).Starch suspensions (9%, w/w; dry starch basis, 28 g total weight) were equilibrated at 30°C for 1min, heated at 95°C for 5.5 min, at a rate of 6°C /min, held at 95°C for 5.5 min, cooled down to 50°C at a rate of 6°C/min and finally held at 50°C for 2 min. It was a programmed heating and cooling cycle. Parameters recorded were pasting temperature (PT), peak viscosity (PV), minimum viscosity (MV), or trough viscosity (TV), final viscosity (FV), and peak time (PTime). Breakdown viscosity (BV) was calculated as the difference between PV minus MV, while total setback viscosity (SV) was determined as the FV minus MV. All determinations were performed in triplicate and expressed in rapid viscosity units (RVU).

Statistical analysis

Experimental data were analyzed statistically using Microsoft Excel and SPSS V. 12 .0.

RESULTS AND DISCUSSION

Yield and gross chemical composition of starches

The yield and gross chemical composition of the two isolated rice starches, that is, Ilaje rice starch (ILRS) and Igbemo rice starch (IGRS), and two isolated cowpea starches, that is, white cowpea starch (WCS) and brown cowpea starch (BCS) are shown in Table 1. The starch yield range from 38.00 to 48.40%, the values for the cereal starches were higher than that for the legume starches for obvious reasons. The starch component of cereal is generally higher than that of legume; additionally starch isolation from legume is made more arduous due to the presence of highly hydrated fine fiber fraction (Vose, 1977) which is derived from the cell wall enclosing the starch granules. The starch yield for the cereals could have been higher if not for the four proteins (albumin, globulin, prolamin and glutelin) that are strongly associated with the starch in rice endosperm and small granules of rice starch that are slow to settle in aqueous medium, with the resultant losses during separation and purification. The starch yield for the cereals (ILRS and IGRS) is in accordance with works reported on long-grain rice starch from Houston, Texas, by other researchers (Wang and Wang, 2004). Legume starch (WCS and BCS) (Table 1) yield falls within the range reported in the literature for most legume starches (Hoover and Sosulski, 1991) but higher when compared to some other legume starches such as beach pea (*Lathyrus maritimus*) (12.30%), grass pea (*Lathyrus sativus*) (26.00%), green pea (*Pisum sativum*) (30.00%) (Chavan et al., 1999) and adzuki bean (*Vigna angularis*) (21.50%) (Naivikul and D'Appolonia, 1979). Brown cowpea (BC) has the lowest starch yield while ILR has the highest.

The significant variation in moisture content (10.18 to 12.77%) of the starches might be attributed to differences in cultivars (Chen et al., 2003). The values of the moisture content for starches (both cereal and legume) concur with the established goal necessary to reach a stable shell life (less than 14% moisture content (Juliano and Villareal, 1993). Values obtained for moisture content of the cereal starches agree with those reported in the literature by Huaisan et al. (2009) and Li et al. (2008). Moisture content (10.90 to 12.77%), lipid content (0.10 to 0.50%) and residual protein content (0.42 to 0.43%) of isolated rice starches (ILRS and IGRS) are similar to that previously obtained by Li et al. (2008).

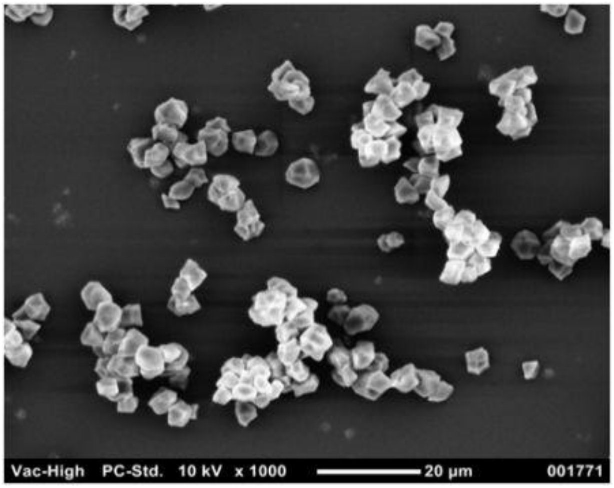
There are significant differences ($P < 0.05$) between the residual protein content (RPC) of the cereal starches and the legume starches (Table 1). The higher RPC of the cereal starches might be due to the fact that some of the proteins were not soluble in the alkali (NaOH) used for their extractions. Poor solubility of prolamin in NaOH and the high solubility of glutelin, globulin and albumin in NaOH had been previously reported (Cardoso et al., 2007a; Cardoso et al., 2007b). It could be rationalized that most of the RPC in rice starches are prolamin, especially when they are alkali-isolated. There are no significant differences ($P < 0.05$) between the RPC, fat content and ash content of the legume starches (WCS and BCS) (Table 1) and this is in agreement with literature values for other legume starches, such as adzuki bean (*Vigna angularis*) starch and lima bean (*Phaseolus lunatus*) starch (Tjahjadi and Breene, 1984; Betancur-Ancona et al., 2003). The low ash (elemental composition) content and low RPC of the legume starches are indication of the purity of the starches obtained in this work. The significant differences in lipid and ash contents between cereal and legume starches could be attributed to differences in biological source, soil type during growth (Morrison and Azudin, 1987), environmental and cultural practices (Sujatha et al., 2004). High solar radiation during grain development generally reduces protein content (Resurreccion et al., 1997).

Apparent amylose (AAM) concentration differ significantly ($P < 0.05$) in all the four starches (Table 1). The values for the legume starches are higher than that of the cereal starches. AAM content for cowpea starches fall within the range stipulated in the literature (Aremu, 1991). According to the latter investigator, the AAM concentration of starches from cowpea cultivars ranged from 6.920 to 39.30%, averaging at 17.70%. These significant differences in AAM content of rice (cereal) starches and cowpea (legume) starches might be attributed to differences in genotype, environmental conditions, and cultural practice (Kim and Wiesenborn, 1995) and is also affected by the climatic conditions and soil type during growth (Morrison et al., 1984). According to Resurreccion et al. (1997), a higher temperature during growth could result in a lower AM content. Inclusively, the same cultivar grown under different environmental conditions will fall into different amylose groups and the influence of temperature is highly pronounced during the ripening of grains. The AAM content is highest for BCS and lowest for IGRS. The results for AAM content of rice starches are consistent with those reported by Jane et al. (1999). Based on the classification of rice starch by AM content (Juliano, 1992), ILR and IGR starches are intermediate (20 to 25%). Typically for legume starches, these values (27.06 and 29.53%) of AAM content for WCS and BCS are somewhat intermediate because lower and higher values of AAM contents have been reported for other legume starches in the literature. It is absolutely necessary to point out the difficulties involved in an attempt to compare lipid values in legume starches, because different extractants were utilized by different researchers (Kawano et al., 1989). These different lipid extractants differ in their ability to extract firmly bound lipids (Vasanthan and Hoover, 1992) and become obviously difficult to compare results from published data. Infact, the literature is replete with conflicting information with respect to the amylose and lipid contents of legume starches.

Morphological properties of starch granules

Scanning electron micrographs of the four isolated starches are shown in Figure 3a to k. The granule morphology was significantly different from each other. The rice starch (ILRS and IGRS) granules are smaller in size than the cowpea starches. They are irregular, polygonal and angular-shaped (Figure 3a to f). In contrast, the legume starch (WCS and BCS) granules (Figure 3g to k) have unequal shapes and sizes which varied from round to ellipsoid. Identical morphology had been reported for other legume starch granules (Singh et al., 2004; Hoover and Sosulski, 1991).

The SEM of the two alkali-isolated rice starches showed individual granules and compound granules. The discrepancies in the images are the variations in the numbers of individual and compound granules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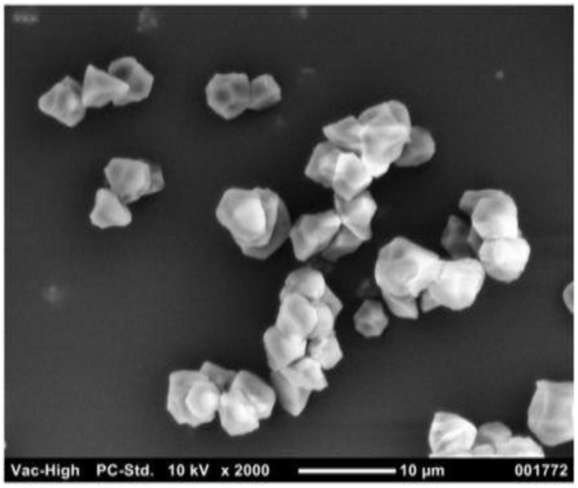
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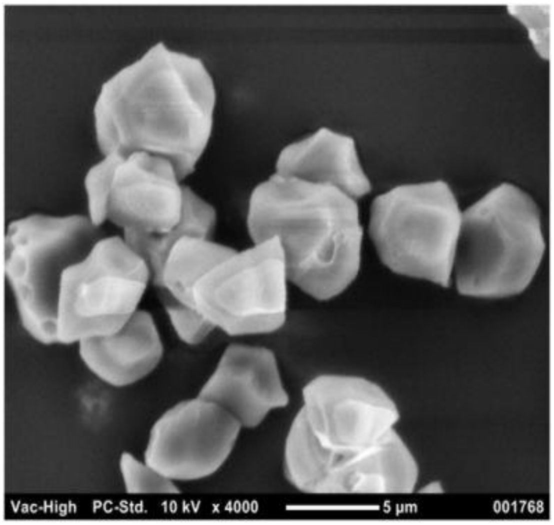
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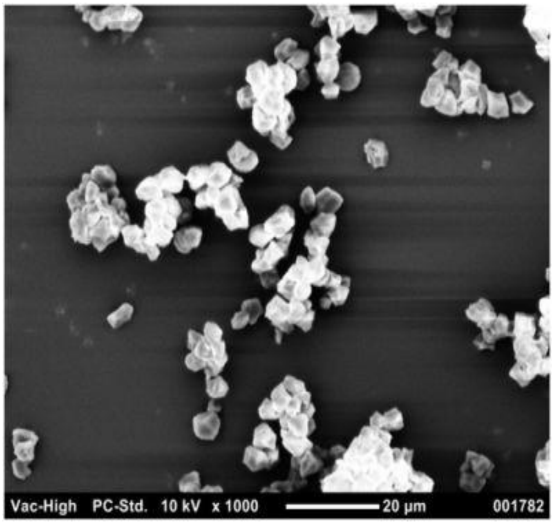
c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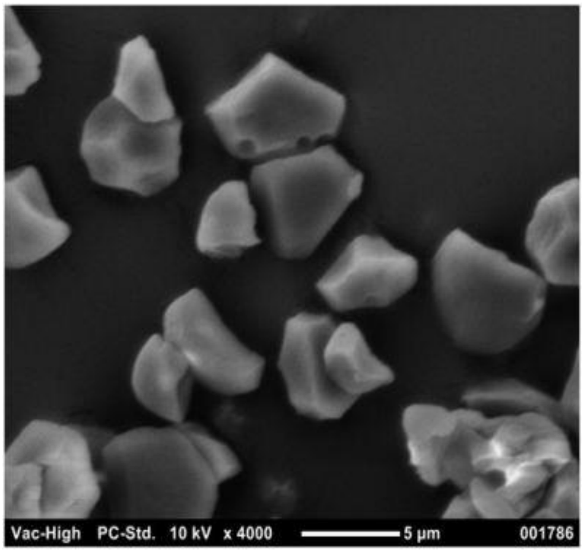
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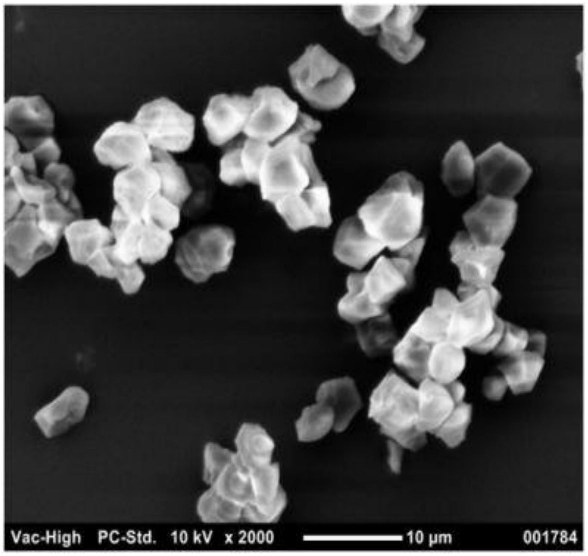
e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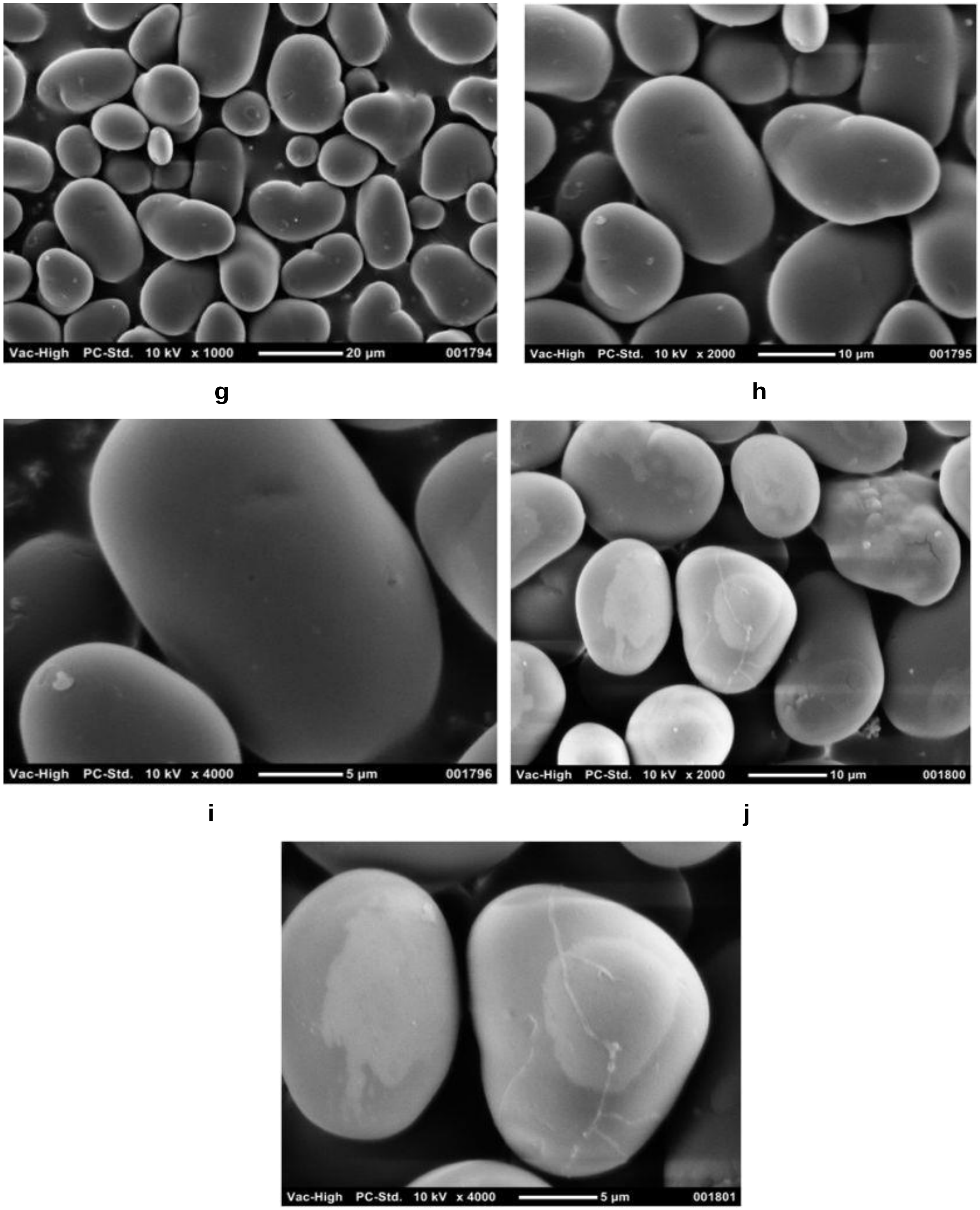
f



g h

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k

Figure 3. (a) SEM micrographs of ILRS granules (Mag. X 1000); (b) SEM micrographs of ILRS granules (Mag. X 2000); (c) SEM micrographs of ILRS granules (Mag. X 4000); (d) SEM micrographs of IGRS granules (Mag.X 1000); (e) SEM micrographs of IGRS granules (Mag. X 2000); (f) SEM micrographs of IGRS granules (Mag. X 4000); (g) SEM micrographs of WCS granules (Mag. X 1000); (h) SEM micrographs of WCS granules (Mag. X 2000); (i) SEM micrographs of WCS granules (Mag. X 4000); (j) SEM micrographs of BCS granules (Mag. X 2000); (k) SEM micrographs of BCS granules (Mag. X 4000).

Table 2. Bulk density, dispersibility and pH of starches from cereal and legume.

Cultivars	Bulk density (g/ml)	Dispersibility (%)	pH
ILRS	0.52 ± 0.02^{a}	75.10 ± 0.27^{a}	6.80 ± 0.01^{a}
IGRS	0.48 ± 0.02^{a}	80.02 ± 0.27^{b}	6.90 ± 0.02^{a}
WCS	0.72 ± 0.01^{b}	74.20 ± 0.26^{c}	6.90 ± 0.03^{a}
BCS	0.75 ± 0.02^{b}	72.10 ± 0.24^{d}	6.90 ± 0.03^{a}

Uncommon superscripts along columns indicate statistically significant difference ($P<0.05$).

(Figure 3a to f). This granule clustering had been reported for rice starch granules (Ashogbon and Akintayo, 2012a, b). Compound granules formation were attributed to the presence of residual protein as indicated by Cardoso et al. (2006) or due to the drying conditions that produce slight gelatinization on the surface of granules to adhere together to form aggregates as proposed by Newman et al. (2007). It seems the contribution of residual protein is more than that of gelatinization in the formation of compound granules. On the other hand, formation of compound granule was not showed by the cowpea starches. Although, granules clustering had been reported in some legume starches, such as beach pea (*Lathyrus maritimus*), green pea (*Pisum sativum*), and grass pea (*Lathyrus sativus*) (Chavan et al., 1999).

Alkali gelatinization depends on the concentration of the alkali (NaOH). Since these rice starches were extracted at low alkali concentration (0.1% NaOH), the occurrence of the phenomenon of alkali gelatinization was completely ruled out. This position is clearly in consonance with that of Cardoso et al. (2007a) which state that progressive loss of granules morphology due to alkali gelatinization is likely to occur when treatment of the rice flour is done with NaOH concentration higher than 0.24% (w/v). Alkali gelatinization is unlikely to be responsible for compound granules formation in this work and lack of clustering in cowpea starch granules might probably be due to their very low residual protein content.

It seems more compound granules are formed by ILRS when compared to IGRS (Figure 3c and f). There is also insignificant difference in their residual protein content, with ILRS having the upper edge. There are important discrepancies in the shape of the two cowpea starch (WCS and BCS) granules. The surface of WCS granules appeared smooth and showed no evidence of fissures (Figure 3g to i). Identical morphological manifestation was reported for pea starch granules (Miao et al., 2009; Ratnayake et al., 2001). In contrast, BCS granules were less regular and ellipsoidal with a frontal bulge (Figure 3j and k). The actual cause of the individual characteristics and morphologies of the starch granules are not known, but obvious factors are genetical control, types and amounts of the starch molecules, membrane structures of the amyloplast organelle, arrangement and association of starch molecules (Jane et al., 1994).

Functional properties of rice and cowpea starches

The values for bulk density, dispersibility and pH are summarized in Table 2. The bulk densities of the four starches ranged from 0.48 to 0.75 g/ml. It is higher for the legume starches (WCS and BCS) when compared to the cereal starches (ILRS and IGRS) (Table 2). Bulk density is essentially a measure of the degree of coarseness of the sample. This means that the particles of the legume starches are coarser than that of the cereal starches. Dispersibility is a measure of reconstitution of starch flour in water, the higher the dispersibility, the better the flour reconstitutes in water (Kulkarni et al., 1991). The dispersibility of the isolated starches ranged from 72.10 to 80.02%, the highest value was for IGRS and the lowest value for BCS. Since the higher the dispersibility the better the starch flour reconstitutes, the values obtained for the cereal starches (75.10 and 80.02%).

(Table 2) were better than those of the legume starches. Furthermore, these values are better than the 40.67% obtained by Akanbi et al. (2009) for breadfruit starch. pH is an important property in starch industrial applications, being used generally to indicate the acidic or alkaline properties of liquid media. There are no significant differences in the pH values (Table 2) of the four isolated starches. They all have very low acid value. Lower pH values of starch dispersions have been reported (pH of 3.71 to 3.99) (Ahmed et al., 2007).

The values for swelling power (SP) (g/g) and water solubility index (WSI) (%) for the cereal starches and legume starches are summarized in Tables 3 and 4. The SP of the cereal starches (ILRS and IGRS) started to rise drastically at 65°C, but the SP of IGRS was higher than that of the ILRS. This is probably due to the higher AP content of IGRS. In contrast, there was a gradual increase in the SP of the cowpea starches as the temperature increases. Generally, the higher SP for the cereal starches when compared to the legume starches might be due to their higher AP content. IGRS with the smallest apparent amylose (AAM) content had the highest SP during heating.

The data were identical to those reported in the literature by Lii et al. (1995) and Yeh and Li (1996). On the other hand, legume starches (WCS and BCS) with the higher AAM had the lower SP when compared to the cereal starches. Similar trend in the gradual increase in

Table 3. Temperature (°C) effects on SP (g/g) of starches.

Cultivars	Swelling power with different temperature				
	55°C	**65°C**	**75°C**	**85°C**	**95°C**
ILRS	2.93 ± 0.12	9.16 ± 0.13	10.18 ± 1.17	11.92 ± 1.17	29.2 ± 1.20
IGRS	3.68 ± 0.11	17.32 ± 0.25	19.36 ± 0.13	22.31 ± 1.16	32.45 ± 1.18
WCS	1.85 ± 0.13	2.07 ± 0.16	4.88 ± 0.17	5.22 ± 0.25	6.48 ± 0.23
BCS	1.66 ± 0.11	2.07 ± 0.12	5.86 ± 0.12	6.59 ± 0.24	7.85 ± 0.22

Table 4. Temperature (°C) effects on WSI (%) of starches.

Cultivars	Water solubility index with different temperature				
	55°C	**65°C**	**75°C**	**85°C**	**95°C**
ILRS	0.42 ± 0.13	2.12 ± 0.16	2.78 ± 0.23	4.10 ± 1.12	18.11 ± 1.22
IGRS	0.91 ± 0.12	3.95 ± 0.24	8.53 ± 0.24	11.05 ± 0.25	11.59 ± 1.12
WCS	0.29 ± 0.16	0.57 ± 0.12	1.09 ± 0.23	4.28 ± 0.11	1.60 ± 0.13
BCS	0.53 ± 0.17	0.28 ± 0.13	1.16 ± 0.24	1.58 ± 0.13	2.75 ± 0.14

Table 5. Pasting properties of starches from cereal and legume.

Cultivar	PV (RVU)	TV (RVU)	BV (RVU)	FV (RVU)	SV (RVU)	Peak time (min)	PT (°C)
ILRS	279.69 ±0.2^{a}	227.10 ± 0.1^{a}	52.59 ± 0.1^{a}	301.17 ± 0.2^{a}	74.07 ± 0.2^{a}	6.78 ± 0.2^{a}	61.20 ± 0.1^{a}
IGRS	220.50 ± 0.1^{b}	173.10 ± 0.1^{b}	47.40 ± 0.1^{b}	223.67 ± 0.1^{b}	50.57 ± 0.1^{b}	6.68 ± 0.2^{a}	62.10 ± 0.1^{b}
WCS	451.67 ± 0.1^{c}	236.58 ± 0.1^{c}	215.09 ± 0.1^{c}	313.75 ± 0.1^{c}	77.17 ± 0.1^{c}	4.43 ± 0.1^{b}	50.30 ± 0.1^{c}
BCS	474.83 ± 0.2^{d}	266.75 ± 0.1^{d}	208.08 ± 0.1^{d}	358.33 ± 0.1^{d}	91.58 ± 0.2^{d}	4.50 ± 0.1^{b}	50.20 ± 0.2^{c}

PV, peak viscosity; TV, trough viscosity; BV, breakdown viscosity; FV, Final viscosity; SV, Setback viscosity; PT, pasting temperature. Uncommon superscripts along columns indicate statistically significant difference ($P < 0.05$).

SP with increasing temperature in WCS and BCS had also been indicated by Henshaw and Adebowale (2004) for starches from other cowpea cultivars; by Ratnayake et al. (2001) for field pea starches and by Chavan et al. (1999) for beach pea starches. The WSI of the cereal starches increased as the temperature increased. It is a bit difficult to rationalized the WSI of the legume starches, but there was a gradual increase in WSI of WCS as the temperature increases till 85°C (Table 4), after this, there was a decrease in WSI. In the BCS, there was an initial decrease in WSI at 65°C, after which, there was a gradual increase in WSI as the temperature increases. The difference in SP among the isolated four starches indicates variation in the strength of associative bonding forces within its granules (Leach, 1959). The highest SP shown by IGRS might be indicative of weak bonding forces within its granules and the fact that it is less compact when compared to the other starch granules. The difference in AAM content and starch granular properties may also have affected SP and solubility of the starches (Singh and Singh, 2001). Starch granules become increasingly susceptible to shear disintegration as they swell and starches with lower AAM content (higher AP content) swell more than those with higher AAM content. This is corroborated by the work of Tester and Morrison (1990) which reported that AP contributes to swelling of starch granules and pasting, whereas AM and lipids inhibit swelling. Unlike the cereal starches, the trace amount of lipids in the legume starches might have not affected its SP.

Starch pasting properties

The pasting characteristics of the cereal starches and the legume starches are shown in Table 5. PT of the starches varies significantly ($P < 0.05$) and ranged from 50.20 to 62.10°C. Legume starches had lower PT when compared to cereal starches (Table 5). But for rice starches, PT range from 79.10 to 79.50°C has been previously reported (Huaisan et al., 2009). In contrast, PT range of 50.20 to 52.50°C for black gram (*Vigna mung*), chickpea (*Cicer arietinum*), field pea (*Pisum sativum*), lentil (*Lens culinaris*), mung bean (*Phaseolus aureus*), and pigeon pea (*Cajanus cajan*) starches studied by Sandhu and Lim (2008) concurs with our study of cowpea starches (WCS and BCS). Higher PT values for legume starches were reported by some researchers: identical values of 79.50°C for four cultivars of field pea starches (Ratnayake et al., 2001); and a range of 75.80 to 80.30°C for some Indian black gram starches (Singh et al., 2004). The lower PT of cowpea starches when compared to rice starches may be attributed to their lower resistance towards swelling.

PV (the highest viscosity attainable during heating) corresponds to the point when the numbers of swollen, but still intact starch granules are maximal, it indicates the water binding capacity of the starch granules (Shimelis et al., 2006) and it also frequently correlated with final product quality. Cereal starches presented lower PV values than the legume starches, and the PV values of the latter were obtained at lower temperatures. PV value was found to be lowest for IGRS (220.50 RVU) and highest for BCS (474.83 RVU) (Table 5). However, BCS showed the lowest PT (50.20°C), compared with 62.10°C of the IGRS. It indicates that the BCS has the highest water-holding capacity of the starches (Sekine, 1996), and could develop large PV at a low PT. It can also swell more freely than the other starches. Maximum PV also reflects the capacity of starch granules to swell freely before physical breakdown or rupture as a result of higher temperature and mechanical agitation. Shibanuma et al. (1996) reported that the properties of starch dispersion were more affected by the chain-length distribution of AP than by the molar mass. Additionally, viscosities during pasting are very much affected by the AM/AP ratio (Biliaderis, 1991).

PV is accompany immediately by a reduction in viscosity to a minimum (TV), due to rupture of the starch granules and leaching of the lower molecular weight glucan polymers, e.g., AM, as a result of exposure to higher temperature and shear. The BV is a measure of the vulnerability of cooked starch to disintegration. BV ranged between 47.40 and 215.09 RVU (Table 5), the lowest for IGRS and the highest for WCS. The values of BV of the starch samples vary significantly ($P < 0.05$). The higher the breakdown in viscosity, the lower is the ability of the starch sample to withstand heat and shear stress during cooking. Therefore, ILRS (52.59 RVU) and IGRS (47.40 RVU), both cereal starches might be able to withstand more heat and shear stress compared to BCS (208.08 RVU) and WCS (215.09 RVU) because of their lower breakdown values. These cowpea starches (WCS and BCS) possess less ability to resist heat and shear stress when compared to rice starches. Identical results were reported for starches from 13 improved Indian black gram cultivars (Singh et al., 2004) due to their higher BV values.

Setback is a measure of recrystallization of gelatinized starch during cooling or setback value is the recovery of the viscosity during cooling of the heated starch suspension. There are significant differences in the values of SV for the isolated starches. BCS with the highest AAM (Table 1) concentration shows the highest SV value; in contrast IGRS with the lowest AAM concentration (Table 1) has the lowest SV value (Table 2). This is in absolute agreement with works in the literature (Gudmundsson, 1994) that constantly link high AAM concentration with the tendencies of syneresis and retrogradation, especially in legume starches (Ashogbon et al., 2011; Adebowale and Lawal, 2003). The difference in SV or retrogradation among different starches (rice and cowpea starches) may be due to the amount and the molecular weight of AM leached from the granules and the ghost of the gelatinized starch granules (Loh, 1992). The increase in viscosity due to the cooling of the gelatinized starch (including leached components and the granule ghost) resulted from network formation between AM and AP while retaining a certain amount of water (Gimeno et al., 2004) and finally resulting in a characteristic gel.

FV (indicate the ability of the starch to form a viscous paste) for different starches ranged from 223.67 to 358.33 RVU (Table 5), the lowest shown by IGRS and the highest by BCS. The increased FV for the legume starches (BCS and WCS) when compared to the cereal starches (ILRS and IGRS) indicate that their paste could easily form a more rigid gel (Zhang et al., 2005). Moreover, high-AM (linear) starches reassociate more readily than high-AP (branched) starches. This indicated that the legume starches (especially BCS) were more prone to retrograde than cereal starches during the cooking processes, followed by gradual cooling. It had been reported by Miles et al. (1985) that an increase in FV might be due to the reassociation of AAM molecules. In contrast, Juliano et al. (1987) attributed differences in pasting characteristics of starches to the difference in AP molecular structure rather than AAM. It is also possible that the differences in the degree of randomly limited branching in AAM concentration might have also contributed to varietal differences (Ashogbon and Akintayo, 2012a). Other reasons for differences may be inherent differences in starch structure or may be due to different degree of interactions between starch and its associated compounds during pasting (Zhang and Hamaker, 2008).

CONCLUSIONS

The variation in the yield, composition, morphology and functional properties of starches from rice and cowpea cultivars were studied. The highest starch yield was from Ilaje rice and the lowest from brown cowpea grain. The residual protein, fats, and ash contents of the rice starches were higher than that of the cowpea starches, an obvious indication that the cowpea starches were purer than the rice starches. BCS showed the highest apparent amylose (AAM) content and lowest residual protein content, in contrast IGRS had the lowest AAM content. The tendency to retrograde will be more pronounced in the legume (cowpea) starches because of their higher AAM concentration. There were no significant differences in the pH of the four isolated starches, but the higher dispersibility and lower bulk density of the cereal starches when compared to the legume starches mean that the cereal starches possessed smaller particles and were capable of reconstituting better in aqueous medium than the legume starches. Both the swelling power (SP) and water solubility index (WSI) of the isolated starches differ significantly. The SP increased with increasing temperature for all the starches, although it was more pronounced for the rice starches. The WSI increased with increasing temperature for the rice starches, but there was inconsistency in the WSI values of the cowpea starches with increasing temperature. Significant differences were observed in the individual pasting parameters. Cooked BCS had the highest peak viscosity. With the exception of pasting temperature and peak time, all the other pasting parameters were higher for the cowpea starches when compared to the rice starches. Varietal differences in pasting properties were attributed to the differences in amylopectin molecular structure rather than the amylose. The composition and pasting properties of these starches indicate that they can be used in the food industry and non-food applications such as in paper, pharmaceutical and textile industries.

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