

A review on isolation, composition, physicochemical properties and modification of Bambara groundnut starch



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ABSTRACT

Bambara groundnut is leguminous crop indigenous to Africa. The major component in Bambara groundnut is starch. Due to the growing demand for starch by the industry, researchers are now focusing on underutilised crops such as Bambara groundnut as possible source of starch for various industrial applications. This review summarizes the present knowledge on the isolation, composition, physicochemical properties and modification methods of Bambara groundnut starch. Future studies are also suggested for value addition and improved utilization of the grain.

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1. Introduction

Bambara groundnut (*Vigna subterranea*) is a leguminous crop grown in many parts of Africa. The name, Bambara groundnut was derived from the name of a Mali tribe called “Bambara” (Murevanhema & Jideani, 2015; Yao et al., 2015). Bambara groundnut is a hardy crop which can grow under extreme drought conditions (Poulter, 1981) and thus, well adapted to the changing climate (Oyeyinka, Singh, Adebola, Gerrano, & Amonsou, 2015). The annual production of Bambara groundnut is about 330,000 tonnes. Of these tonnage, 45–50% is produced in West Africa with Nigeria being the world leading producer with about 33,000–49,000 tonnes annually (Bamshaiye, Adegbola, & Bamishaiye, 2011). According to previous research, Bambara groundnut exists mainly as landraces with few varieties developed through controlled breeding (Aliyu, Massawe, & Mayes, 2016; Massawe, Dickinson, Roberts, & Azam-Ali, 2002). Research efforts in many parts of Africa including Southern Africa on Bambara groundnut have shown successful breeding on this crop to facilitate production of high yielding accessions (Oyeyinka et al., 2015; Shegro, van Rensburg & Adebola, 2013). The grains of Bambara groundnut come in different shape, size and colour (Fig. 1) (Oyeyinka, 2017). According to a Document published by the Department of Agriculture Forestry and Fisheries, Bambara groundnut has seven varieties differentiated by their colour ranging from black, red, cream/black (AFF, 2011).

The microstructure of Bambara groundnut grain (Enwere & Hung, 1996) is similar to those reported for cowpea (Avanza, Chaves, Acevedo, & Añón, 2012; Sefa-Dedeh & Stanley, 1979; Sefa-Dedeh, Stanley, & Voisey, 1978) and African yam bean (Enwere, Hung, & Ngoddy, 1990). Cross sections of cowpea revealed the presence of different shapes and sizes of starch granules in parenchymatous cells (Fig. 2) embedded in a compact protein matrix (Avanza et al., 2012). A similar arrangement of starch granules has been reported for Bambara groundnut (Enwere & Hung, 1996). Microstructure of Bambara groundnut cotyledon revealed that the matrix contained smooth surfaced starch granules embedded within the cell wall (Enwere & Hung, 1996).

Grain compositional data reported for Bambara groundnut (Adebowale, Afolabi, & Lawal, 2002; Arise, Amonsou, & Ijabadeniyi, 2015; Oyeyinka et al., 2015; Sirivongpaisal, 2008) appears very similar to those reported for cowpea (Aremu, Olaofe, & Akintayo, 2006a; Henshaw, 2008; Oyeyinka et al., 2013). Bambara groundnut is mainly composed of carbohydrate (57–67%) and proteins (15–27%) (Adebowale et al., 2002; Arise et al., 2015; Oyeyinka et al., 2015; Sirivongpaisal, 2008). Bambara groundnut seed is often referred to as a complete food because of its

reasonably high protein content (Adebowale et al., 2002; Arise et al., 2015; Oyeyinka et al., 2015; Sirivongpaisal, 2008) and a good balance of the essential amino acids (Yao et al., 2015). The protein of Bambara groundnut contains high levels of lysine (6.5–6.8%) and considerable amount of methionine (1.8–2.84%) which is normally limiting in most legumes (Aremu, Olaofe, & Akintayo, 2006b; Kudre, Benjakul, & Kishimura, 2013; Steve Ijarotimi & Ruth Esho, 2009). Bambara groundnut is very low in fat, usually less than 10% and that classifies the grain as a pulse. According to Minka and Bruneteau (2000), linolenic, palmitic and linoleic acids are the predominant fatty acids in Bambara groundnut with average values of 21, 30 and 44%, respectively. Stearic acid was found in small quantities (approx. 6%) in the grains (Minka & Bruneteau, 2000). Other report on fatty acid profile of Bambara groundnut showed that almost half of the lipid content (47.4%) is composed of saturated fatty acids (12:0–18:0), and the other half (48.3%) is composed of unsaturated fatty acids (18:1–18:3) (Nwokolo, 1987). Differences in compositional data reported for Bambara groundnut may be attributed to several factors such as growth stage of plant, plant cultivar environmental conditions and genotypic differences.

Bambara groundnut has been used in making different products such as puddings (Ukegbu & Uwaegbute, 2014) snack (*kangu*) (Adefalu & Fawole, 2014), vegetable milk (Brough, Azam-Ali, & Taylor, 1993; Murevanhema & Jideani, 2015) and low fat yoghurt (Falade, Ogundele, Ogunshe, Fayemi, & Ocloo, 2015). Other reports showed that Bambara groundnut protein hydrolysate and peptide fractions may be potentially used as ingredients in the formulation of functional foods and nutraceuticals against high blood pressure and oxidative stress (Arise et al., 2016; Arise et al., 2017). Bambara groundnut is also a good source of starch (18 and 45%), which may be potentially used as a starch source for the industry (Kaptso et al., 2014; Oyeyinka, Singh, & Amonsou, 2016a; Oyeyinka, Singh, Ying, & Amonsou, 2016d; Oyeyinka et al., 2015). However, Bambara groundnut remains an underutilised crop. The underutilization of Bambara groundnut may be attributed to the hard-to-cook defect that increases time of processing (Alozie, Iyam, Lawal, Udofia, & Ani, 2009) as well as limited research available on the crop (Oyeyinka et al., 2015).

With the growing demand of starch by the industry, Bambara groundnut starch may play a role as an alternative and sustainable starch source to the conventional corn and potato sources. These conventional sources are currently used for various industrial applications, but there is less information on Bambara groundnut starch. Thus extracting starch from Bambara groundnut may be a promising step to improve utilization beyond traditional usage. This review summarizes the current studies available in the



Fig. 1. Bambara groundnut with different colour. M: Maroon, B: Brown, C: Cream. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Source: (Oyeyinka, 2017)

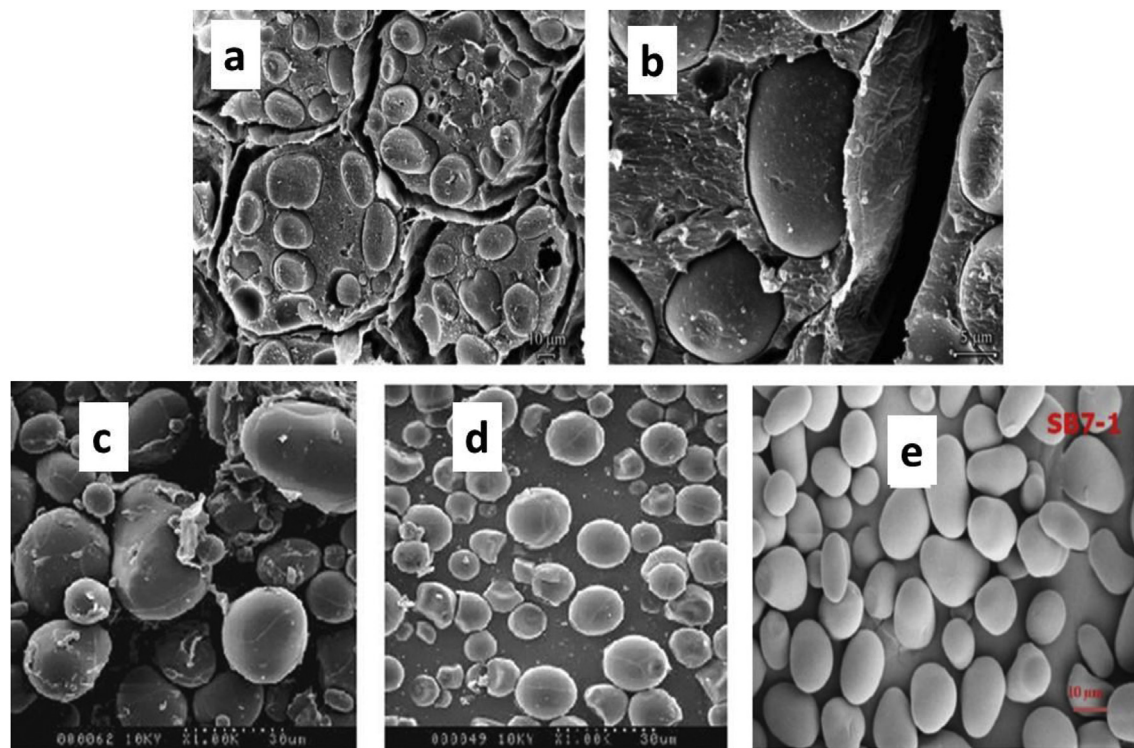


Fig. 2. Micrograph of the cross section of cowpea grains and Bambara groundnut starch.

a: raw cowpea seed (Avanza et al., 2012)

b: cowpea starch granule (Avanza et al., 2012)

c: starch extracted from white Bambara (Kaptso et al., 2014)

d: starch extracted from black Bambara (Kaptso et al., 2014)

e: starch extracted from brown Bambara (Oyeyinka et al., 2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

literature on isolation, composition, physicochemical properties and modification of Bambara groundnut starch.

2. Native starch characterization

2.1. Starch extraction

Starch extraction from legumes can be categorized into dry and wet milling (Hoover, Hughes, Chung, & Liu, 2010). Dry milling is widely used industrially, while wet milling method is mainly used in the laboratory (Hoover et al., 2010). Reported starch extraction method from Bambara groundnut has been by the wet milling (Adebawale & Lawal, 2002; Adebawale et al., 2002; Afolabi, 2012; Oyeyinka et al., 2015; Sirivongpaisal, 2008). However, wet milling method can be categorized further into two types. The first method (method 1) involves extracting starch from processed Bambara groundnut flour, while the other method (method 2) extracts starch from the dehulled grains without drying into flour. Differences in these methods have been found to influence the starch yield from Bambara groundnut. Afolabi (2012) reported approximately 45% starch yield from Bambara groundnut using method 2, which is substantially higher than the yield (18–35%) reported by other researchers using method 1 (Adebawale et al., 2002; Oyeyinka et al., 2015, 2016a). The variety of grain may also influence the starch yields. For example, Poulter (1981), working with eight cultivars of Bambara groundnut grown in the same environment in Ghana observed variations in their starch yields (33–50%). Oyeyinka et al. (2016a), similarly found variations in the starch yield (28–35%) of Bambara groundnut grown in the same environment.

2.2. Starch composition and purity

Starch is composed mainly of amylose and amylopectin. These two starch components account for approximately 98–99% of starch (dry weight) (Tester, Karkalas, & Qi, 2004). Starch functionality is greatly influenced by the ratio of amylose and amylopectin and the amounts of these components may vary with the botanical origin and variety of the grain. Significant variation in the amylose contents (approx. 20–35%) (Table 1) of starches isolated from different Bambara groundnut has been observed (Kaptso et al., 2014; Oyeyinka et al., 2015, 2016a; Sirivongpaisal, 2008). The amylose content of Bambara groundnut starch is comparable to those reported for normal corn (24.8–25.1%) and potato (14.9–23.2%) starches (Joshi et al., 2013; Li & Yeh, 2001). Other factors such as the method of amylose determination and the physiological state of the seed may also influence the amylose content of starch (Hoover et al., 2010). The iodine binding method has been widely used to determine the amylose content of Bambara groundnut starch. However, future studies may use well established chromatographic methods to determine the amylose content of Bambara groundnut starch.

Starch may show the presence of lipids, proteins, and ash, which are present in minute quantities. These minute components are frequently used as an index of starch purity (Maaran, Hoover, Donner, & Liu, 2014; Piecyk, Drużyńska, Worobiej, Wołosiak, & Ostrowska-Ligęza, 2013) and may significantly affect starch functionality (Srichuwong & Jane, 2007). Differences in the composition of these minor components in Bambara groundnut starches has been reported (Adebawale et al., 2002; Afolabi, 2012; Sirivongpaisal, 2008). The protein (0.61–2.30%), lipid

Table 1

Yield and composition of Bambara groundnut starch.

Bambara groundnut seed coat colour	Starch yield (%)	Amylose content (%)	Method of determination	Protein (%)	Lipid (%)	Ash (%)	Reference
Not specified	37.50	NR	NR	1.00	0.08	0.04	(Adebowale et al., 2002)
Not specified	40.35	NR	NR	1.22	0.56	0.49	(Afolabi, 2012)
Not specified	38.20	NR	NR	2.30	1.20	0.50	(Adebowale & Lawal, 2002)
Not specified	33.4–49.5	NR	NR	NR	NR	NR	(Poulter, 1981)
Not specified	45.57	21.67	Iodine binding	0.61	0.44	0.47	(Sirivongpaisal, 2008)
White	NR	25.0	Iodine binding	1.10	0.10	0.20	(Kaptso et al., 2014)
Black	NR	27.8	Iodine binding	0.90	0.10	0.10	(Kaptso et al., 2014)
Not specified	22.0–33.0	19.6–35.1	Iodine binding	NR	NR	NR	(Oyeyinka et al., 2015)
Maroon, Brown, Cream	28.0–35.0	31.5–32.9	Iodine binding	NR	NR	NR	(Oyeyinka et al., 2016a)

NR: Not reported.

(0.08–1.20%) and ash (0.04–0.50%) contents of Bambara groundnut starch are generally low (Table 1). Pulses are generally low in lipids compared to oil seeds. Thus, residual lipid contents in pulse starches such as Bambara groundnut is usually very low and may result in negligible or minimal changes in starch functionality.

2.3. Granule morphology

The morphology of starch isolated from Bambara groundnut has been widely studied using scanning electron microscopy (SEM) (Table 2). However, some authors reported the use of light microscopy in observing the morphology of Bambara groundnut starch (Adebowale & Lawal, 2002). The starch granule size and shape of Bambara groundnut starch has been found to vary with botanical origin and cultivar of the grains (Adebowale & Lawal, 2002; Kaptso et al., 2014; Oyeyinka et al., 2015, 2016a). Kaptso et al. (2014), observed polygonal shaped granules for starch extracted from white Bambara groundnut cultivar and spherical shaped granules for black cultivar (Fig. 2). According to their report, white Bambara groundnut starch showed a remarkably large granule size (10–35 µm) compared to the black cultivar (6–15 µm) (Kaptso et al., 2014). Other authors reported oval and irregularly shaped starch granules with size ranging between 24 and 29 µm (Oyeyinka et al., 2015, 2016a). In general, the surfaces of starch extracted from Bambara groundnut have been reported to be smooth with no fissures, suggesting that the extracted starches are relatively pure (Oyeyinka et al., 2015, 2016a; Sirivongpaisal, 2008). Variation in the morphology of Bambara groundnut starch may depend on plant cultivar, growth stage of plant, environmental conditions, extraction and purification methods.

2.4. X-ray diffraction and degree of crystallinity

Starch may exhibit different crystallinity pattern, depending on the botanical origin and the arrangement of the crystalline lamellae

of amylopectin (Jenkins & Donald, 1995). In general, there are A- or B-type polymorph. The A and B crystalline patterns are differentiated based on the packing arrangement of double helices within amylopectin and their level of hydration (Imberty & Perez, 1988). The A-type is closely packed and are less hydrated, while the B-type has a more hydrated helical core (Cheetham & Tao, 1998; Imberty & Perez, 1988). The C-type polymorph is generally considered as a mixture of the A- and B-types (Pérez et al., 2010). X-ray diffraction studies on Bambara groundnut starch reported the A (Kaptso et al., 2014; Oyeyinka et al., 2016a; Sirivongpaisal, 2008) or C-type pattern (Afolabi, 2012; Oyeyinka et al., 2015). Differences in the crystalline pattern of starches have been attributed to differences in growth conditions, growth locations, and inherent genetic differences among plant species (Agama-Acevedo, Nuñez-Santiago, Alvarez-Ramirez, & Bello-Pérez, 2015; Bello-Perez, Roger, Baud, & Colonna, 1998; Kaptso et al., 2014; Waliszewski, Aparicio, Bello, & Monroy, 2003). The intra or inter granular arrangement of the 'A' and 'B' polymorphs and possibly the proportion of these polymorphs within the starch granule may also influence the XRD reflection. For instance, Bogracheva, Morris, Ring, and Hedley (1998), working with pea starches with the C-type pattern found that the 'A' and 'B' polymorphs are present within a granule, with the B-polymorph located in the center of the granule surrounded by the A polymorph. Furthermore, Gunaratne and Hoover (2002) found that the peak at 5 (2θ) can only be observed above 16% moisture content. Thus differences in starch moisture content may also influence the diffraction pattern of starch.

2.5. Granular swelling

Starch swelling involves interaction between the crystalline and amorphous regions of starch (Hoover, 2001; Singh, Singh, Kaur, Sodhi, & Gill, 2003). Differences in the swelling ability of Bambara groundnut starch has been reported (Adebowale et al., 2002; Afolabi, 2012; Oyeyinka et al., 2015, 2016a; Sirivongpaisal,

Table 2

Morphology, X-ray diffraction pattern and degree of crystallinity of Bambara groundnut starch.

Bambara groundnut seed coat colour	Granule size (µm)	Measuring method	Shape description	Diffraction pattern	Degree of crystallinity (%)	Reference
Not specified	NR	NR	NR	C	38.75	(Afolabi, 2012)
Not specified	18–36	LM, SEM	Predominantly oval, Few granules were concave and round	NR	NR	(Adebowale & Lawal, 2002)
Not specified	45.57	SEM	Oval, round	A	43.7	(Sirivongpaisal, 2008)
White	10–35	SEM	Irregular, polygonal	A	41.1	(Kaptso et al., 2014)
Black	6–15	SEM	Spherical	A	40.4	(Kaptso et al., 2014)
Not specified	26	SEM	Oval, few round and irregular	C	29.4–35.3	(Oyeyinka et al., 2015)
Maroon, Brown, Cream	24–29	SEM	Oval, few round and irregular	A	30.5–33.0	(Oyeyinka et al., 2016a)

LM: Light microscopy, SEM: Scanning electron microscopy.

2008). The variation in the swelling power may be due to variation in amylose contents (Table 1). Oyeyinka et al. (2015) working with starch extracted from five Bambara groundnut genotypes found that low amylose starch showed higher swelling power. However, the dependency of swelling power on the amylose content of starches may vary with the botanical origin and cultivar of the grain. Starch from three Bambara groundnut landraces with significant differences in amylose contents showed similar swelling behaviour (Oyeyinka et al., 2016a). Previous researchers working with starches from different botanical origin similarly found that swelling power may not be expressed as a function of amylose content alone (Li & Yeh, 2001; Naidoo, Amonsou, & Oyeyinka, 2015; Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001). Thus, variation in the swelling power of different starches will depend on many factors such as botanical origin, amylose content, starch granule size, the magnitude of interactions between amorphous and crystalline regions molecular structure of amylose and amylopectin. Compared with potato and corn starches, the swelling power of Bambara groundnut starch appears very low. This may be attributed to different factors. For example, the high phosphate monoester content in potato starch has been reported to contribute significantly to greater hydration and swelling of potato starch granules (Jane et al., 1999; McPherson & Jane, 1999). According to Hoover et al. (2010), pulse starches including those extracted from Bambara groundnut displays a single stage restricted starch swelling and low extent of amylose leaching when compared to cereal starches. The restricted swelling reported in most pulse starches has been suggested to result from the packing arrangement of the amylose chains, which presumably is very close within the amorphous domains of the starch granule (Hoover et al., 2010). Thus, Bambara groundnut starch may be advantageous in food applications where moderate swelling is required.

2.6. Gelatinization properties

Gelatinization involves hydration and swelling of starch granules. The process leads to a phase change of starch granules from an ordered state to a disordered state (Hermansson & Svegmarm, 1996; Hoover et al., 2010). The phase transition occurs in the presence of excess water and over a temperature range specific for starch from different origin. Gelatinization of starch is commonly measured by differential scanning calorimeter (DSC) where starch-water mixture is heated in tightly sealed aluminium pan (Zhu, 2015). The gelatinization properties of starch is generally influenced by amylose content, botanical origin and the structure of amylopectin. Low amylose starch is generally associated with high gelatinization temperature (Kaptso et al., 2016; Kaptso et al., 2014; Naidoo et al., 2015; Stevens & Elton, 1971). Only very few studies (Table 3) reported the gelatinization properties of Bambara groundnut starch (Afolabi, 2012; Kaptso et al., 2014, 2016; Oyeyinka et al., 2016a). Starch extracted from white Bambara groundnut cultivar with low amylose content (25%) reportedly showed high gelatinization temperature of 81.7 °C compared with the black variety (77.5 °C) with higher amylose content (27.8%) (Kaptso et al., 2014, 2016).

Oyeyinka et al. (2016a) similarly found that Bambara groundnut starch with low amylose content displayed higher gelatinization temperature compared to those with higher amylose contents. A substantially higher gelatinization temperature (93.5 °C) was reported for a single variety of Bambara groundnut (Afolabi, 2012). Noda, Takahata, Sato, Ikoma, and Mochida (1996) reported that the onset gelatinization temperature (T_o), peak gelatinization temperature (T_p), conclusion gelatinization temperature (T_c) and the enthalpy of gelatinization (ΔH) of starches are significantly influenced by the structure of amylopectin rather than their amylose content. In general, starches with higher proportion of long amylopectin chains would display high T_o , T_p , T_c and ΔH , while those with abundant short amylopectin chains would exhibit low T_o , T_p , T_c and ΔH (Noda et al., 1996). Huang et al. (2007) associated high gelatinization temperature in cowpea starch with the presence of higher amounts of long amylopectin chains. Experimental conditions such as water to starch ratio and the scanning rate may also influence the hydration of starch granules and their gelatinization behaviour (Freitas, Paula, Feitosa, Rocha, & Sierakowski, 2004; Yeh, Chan, & Chuang, 2009). The influence of the amylopectin chain length in Bambara groundnut starch on starch gelatinization remains unclear. Hence, future studies should be done to characterize the amylopectin distribution in Bambara groundnut starch and determine the influence of the chain length distribution of amylopectin its physicochemical properties.

2.7. Rheological properties

The rheological properties of starch may be studied using non-laminar flow conditions where starch paste is subjected to both thermal and mechanical treatments such as in pasting. However, rheological properties of Bambara groundnut starch has been widely studied using Brabender viscoamylograph (BVA) and rapid visco analyser (RVA) (Table 4). Pasting refers to changes in the starch structure after gelatinization has occurred (BeMiller, 2011; Hoover et al., 2010). The pasting properties of Bambara groundnut starch has been found to vary with the grain source and variety as well as experimental conditions (Adebawale & Lawal, 2002; Adebawale et al., 2002; Oyeyinka et al., 2016a; Sirivongpaisal, 2008).

Pasting temperature of Bambara groundnut starch may vary between 78 and 84 °C depending on the source and variety of the grain (Adebawale et al., 2002; Afolabi, 2012; Oyeyinka et al., 2016a; Sirivongpaisal, 2008). According to Hoover et al. (2010), most pulse starches display a high pasting temperature and this could be associated with their relatively high amylose contents. In comparison with conventional starch sources, the pasting temperatures reported for Bambara groundnut starch are intermediate between those reported for potato starch (66.2–68.6 °C) (Gałkowska, Pycia, Juszczak, & Pająk, 2014; Joshi et al., 2013) and normal corn starch (77–88 °C) (Gałkowska et al., 2014; Joshi et al., 2013).

The peak viscosity of Bambara groundnut starch has been reported in different units (Brabender Unit and Rapid Viscoanalyser unit). Hence, it may be difficult to compare these data. Variations in

Table 3
Gelatinization properties of Bambara groundnut starch.

Bambara groundnut seed coat colour	Starch: water	Scanning rate (°C/min)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	Reference
Not specified	1:4	10	65.7	93.2	130.0	25.2	(Afolabi, 2012)
Not specified	1:4	10	71.7	75.3	79.2	11.7	(Sirivongpaisal, 2008)
White	1:3	5	76.1	81.7	84.8	12.7	(Kaptso et al., 2014)
Black	1:3	5	73.4	77.5	83.1	13.9	(Kaptso et al., 2014)
Maroon, Brown, Cream	1:3	10	68.3–72.0	73.1–77.5	77.4–84.4	12.7–13.6	(Oyeyinka et al., 2016a)

T_o : onset gelatinization temperature, T_p : peak gelatinization temperature, T_c : conclusion gelatinization temperature, ΔH : enthalpy of gelatinization.

Table 4

Pasting properties of Bambara groundnut starch.

Bambara groundnut seed coat colour	Instrument	Starch concentration (%)	Pasting temperature (°C)	Peak viscosity	Setback viscosity	Final viscosity	Reference
Not specified	BVA	10	84	790	1210	2000	^a (Adebowale et al., 2002)
Not specified	BVA	8	75	430	1570	1500	^a (Adebowale & Lawal, 2002)
Not specified	BVA	6	80.5	243	57	202	^a (Sirivongpaisal, 2008)
Not specified	RVA	14	83.20	278.6	166.58	340.75	^b (Afolabi, 2012)
Maroon, Brown, Cream	RVA	11	77.6–80.4	329.3–385.6	104.9–127.1	286.6–339.5	^b (Oyeyinka et al., 2016a)

^a Units measured in Brabender Unit (BU).^b Units measured in Rapid Visco analyser Unit (RVA).

the peak viscosity values may be explained by differences in starch composition e.g. amylose contents. Amylose contents of various starches have been suggested to prevent swelling during pasting by forming a barrier around the granules (Sang, Bean, Seib, Pedersen, & Shi, 2008). However, studies on Bambara groundnut starch found no inverse correlation of peak viscosity with amylose contents (Oyeyinka et al., 2016a). Hence, other factors such as the presence of trace amounts of lipid complexed amylose chains, the strong interaction between amylose–amylose and/or amylose–amylopectin chains and the molecular structure of amylose and amylopectin may influence the peak viscosity of Bambara groundnut starch. Huang et al. (2007), found that cowpea starch exhibited a higher peak viscosity than starches from chickpea and yellow pea due to its higher amount of long amylopectin chains. Other reports on starch functionality found that the distributions of amylopectin chain length of starches from different botanical origin predominantly affected their pasting properties (Jane et al., 1999).

Other rheological studies using a rheometer found that Bambara groundnut starch displayed a pseudo-plastic behaviour typical of macromolecules (Oyeyinka et al., 2015). Amylose content was found to significantly influence the viscosity of Bambara groundnut starch within the studied shear rate range of 10 and 1000 s⁻¹. High amylose starch was reported to correlate with high viscosity, which was attributed to the shear induced during gelatinization process and subsequent solubilization of amylose (Oyeyinka et al., 2015). According to these authors the solubilised amylose enhances the viscosity of Bambara groundnut starch pastes. Future studies may be required to understand the dynamic rheological properties of Bambara groundnut starch gels using frequency sweep measurements.

2.8. *In-vitro* digestibility

Nutritionally, starch may be classified into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) according to the rate of glucose release and its absorption in the gastrointestinal tracts (Englyst, Kingman, & Cummings, 1992). RS is a starch fraction known for beneficial health giving functionality in human system (Alimi, Sibomana, Workneh, & Oke, 2017a; Alimi, Workneh, & Oyeyinka, 2017b). This category of starch is fermented by microbes in the large intestine to form short chain fatty acids, which contributes significantly to intestinal health (Alimi, Sibomana, Workneh, & Oke, 2017a). Depending on the variety of the grains, the RDS (11.5–12.3%) and SDS (15.9–16.9%) contents of Bambara groundnut starch is generally low compared to the RS contents (69.7%–72.6%) (Oyeyinka et al., 2016a). Only three variety of Bambara groundnut, maroon brown and cream of the same origin has been used and it is therefore difficult to make meaningful comparison of the levels of RDS, SDS and RS among Bambara groundnut from different origin. Differences in *in-vitro* digestibility of native starches among and within species have been attributed

to many factors including amylose to amylopectin ratio, granule size, degree of crystallinity, type of crystalline polymorphic form, molecular structure of amylopectin (Hoover et al., 2010). Pulse starches are characterized with relatively high amounts of resistant starch which has beneficial physiological effects (Blazek & Copeland, 2008; Oyeyinka et al., 2016a). The high amount of RS in Bambara groundnut starch suggest the potential of the starch as a functional ingredient in various food applications.

3. Modification

Starches are modified to improve functionality and application in the industry (Kaur, Ariffin, Bhat, & Karim, 2012; Oyeyinka et al., 2016d). Starch modification may be achieved by physical, enzymatic, genetic and chemical methods or a combination of these methods.

3.1. Physical modification

Physical modification methods of starch, which includes annealing (ANN) and heat moisture treatment (HMT) are considered safe compared to chemical methods such as oxidation and acetylation. ANN is performed at a temperature above the glass transition, but below the gelatinization temperature of starch (Jayakody, Hoover, Liu, & Donner, 2009). On the other hand HMT involves treating starch at low moisture levels, usually between 10 and 30% and heating of starch between 90 and 120 °C for time varying time (15 min and 16 h) (Chung, Hoover, & Liu, 2009a; Chung, Liu, & Hoover, 2009b). ANN and HMT of Bambara groundnut starch was found to significantly reduce its swelling power and solubility (Adebowale & Lawal, 2002). The reduction in swelling power following hydrothermal modification has been attributed to internal rearrangement within the starch granules, resulting in stronger interaction among the starch bonding functional groups (Chung et al., 2009a, 2009b; Hoover, Li, Hynes, & Senanayake, 1997). Both ANN and HMT reportedly reduced the peak viscosity of Bambara groundnut starch (Adebowale & Lawal, 2002). According to their report, the peak viscosity reduced with increasing level of moisture in the heat moisture treated starches. Furthermore, the pasting temperature of heat moisture treated Bambara groundnut starch was reported to increase, but ANN did not significantly change the pasting temperature of the starch. The changes in the physiochemical properties of pulse starches following hydrothermal treatment have been attributed to interplay of several factors including amylose content, increased interactions between starch chains, arrangement of amylose within the amorphous domains of starch and possible formation of amylose lipid complexes (Hoover et al., 2010). More studies are required to further understand the influence of hydrothermal treatments on starch from different cultivar of Bambara groundnut.

3.2. Chemical modification

Chemical modification of Bambara groundnut starch has involved oxidation, acetylation and carboxymethylation. Changes in the functional properties of Bambara groundnut starch may vary with the chemical used or the modification method. For example, while hypochlorite oxidation significantly reduced the swelling ability of Bambara groundnut starch (Adebawale et al., 2002), the swelling power significantly increased after acetylation (Adebawale et al., 2002) and carboxymethylation (Afolabi, 2012). The increase in swelling power after carboxymethylation was attributed to the incorporation of carboxyl group into Bambara groundnut starch (Afolabi, 2012). This resulted in a loss of crystallinity (confirmed by the X-ray diffraction) and the subsequent increase in the amorphous region that is hydrophilic (Afolabi, 2012). Setback viscosity of Bambara groundnut starch reduced by approximately 17 and 40% after acetylation and oxidation respectively (Adebawale et al., 2002). The result suggest that oxidized and acetylated Bambara groundnut starch will have reduced retrogradation tendencies. Although the use of chemicals are currently being discouraged in the modification of starch, chemically modified Bambara groundnut starch may be useful for non-food applications in the industry, for example, in the textile and paper industry.

3.3. Modification with lipids

Other modification methods used for Bambara groundnut starch involves the use of naturally occurring like substances such as lipids. The modification of starch with lipids results in the formation of inclusion complexes between added lipids and amylose in starch. These complexes are formed under controlled conditions of moisture, shear and temperature. Amylose is believed to change its configuration from the coil to helix, which allows guest molecules to reside within the cavities of amylose helix (Putseys, Lamberts, & Delcour, 2010). Starch-lipid complexes can be formed during gelatinization of starch in the presence of lipids or may be naturally present in starch (Putseys et al., 2010). The choice of lipids in modification stemmed from the demand of safe foods by consumers and the presence of residues of some chemicals such as epichlorohydrin, and hypochlorite solution used in starch modification. Bambara groundnut starch has been modified with lipids for improved functionality and application (Oyeyinka, Singh, Ma, & Amonsou, 2016b; Oyeyinka, Singh, Venter, & Amonsou, 2016c; Oyeyinka et al., 2016d). Bambara groundnut starch reportedly complexed better with potato and corn starches with (Oyeyinka et al., 2016d) or without the application of high pressure homogenization (Oyeyinka et al., 2016c). The increased complexation of Bambara groundnut with lipid compared to corn and potato starches was attributed to differences in their amylose contents (Oyeyinka et al., 2016b, 2016c, 2016d). More importantly, the degree of polymerization (DP) seems to play a crucial role in complexation, since long amylose chains i.e. high DP has been found to produce high V-amylose yield (Godet, Tran, Colonna, Buleon, & Pezolet, 1995). Homogenization at 100 MPa was found to increase the degree of complexation of Bambara groundnut starch by almost double the complexation obtained without homogenization (Oyeyinka et al., 2016b, 2016d). This was associated with uniform distribution of lipids in starch suspension under the influence of high-pressure (Meng, Ma, Cui, & Sun, 2014) and greater release of amylose from swollen starch granules (Meng et al., 2014). Future studies on Bambara groundnut starch may be required to determine the influence of amylose chain length as well as amylopectin branch chain length on the degree of complexation. This is very important because, evidence that lipids can also

complex with amylopectin molecule of starch has also been documented (Eliasson, Finstad, & Ljunger, 1988; Evans & Haisman, 1980).

3.3.1. Effect of lipids on rheological properties of Bambara groundnut starch

Pasting Bambara groundnut starch with stearic acid, linoleic acid, and lysophosphatidylcholine reportedly produced modified starch with higher thermal stability, increased final viscosity and decreased setback viscosity compared to the unmodified counterparts (Oyeyinka et al., 2016c). Lipid modified Bambara groundnut starches also displayed reduction in digestibility suggesting their potential in formulating foods for the management of diabetes (Oyeyinka et al., 2016c). Furthermore, lipid addition to Bambara groundnut starch was found to produce gels with significant reduction in firmness (Fig. 3) (Oyeyinka et al., 2016c). Recent studies further reported that Bambara groundnut starch can produce non-gelling paste when complexed with fatty acids (Oyeyinka et al., 2016b) or lysophosphatidylcholine (Oyeyinka et al., 2016d). The non-gelling paste was formed when complexed starch was homogenized (Oyeyinka et al., 2016b, 2016d). Non-gelling behaviour of starch paste with added lipids has also been reported for corn starches (D'Silva, Taylor, & Emmambux, 2011; Richardson, Kidman, Langton, & Hermansson, 2004). The reduction in gel firmness was associated with the formation of amylose-lipid complexes (D'Silva et al., 2011; Richardson et al., 2004). Amylose-lipid complexes have been suggested to either prevent the formation or increase the spacing between junction zones. The non-gelling behaviour of homogenized Bambara groundnut starch-lipid complex is highly promising for in frozen foods and desserts for better mouth feel. The addition of lipids such as palmitic, stearic, oleic, linoleic acid and lysophosphatidylcholine to Bambara groundnut starch was found to significantly reduce the storage modulus (G') and loss modulus (G'') of Bambara groundnut starch gels (Oyeyinka et al., 2016b, 2016d). The reduction was highest for saturated fatty acids than with the unsaturated types. For example, the addition of palmitic or stearic acid was found to reduce G' of Bambara groundnut starch by approximately 100% compared with oleic and linoleic acid which showed 20 and 50% reductions in G' respectively (Oyeyinka et al., 2016b). Compared to corn and potato starches, Bambara groundnut starch modified without lipids reportedly had substantially higher G' and G'' (100 times) at the same starch concentration of 10% (Oyeyinka et al., 2016b, 2016d). According to these authors, the variation in rheological properties may be due to the presence of longer amylose chains. Although the authors did attribute the variation in rheological properties among

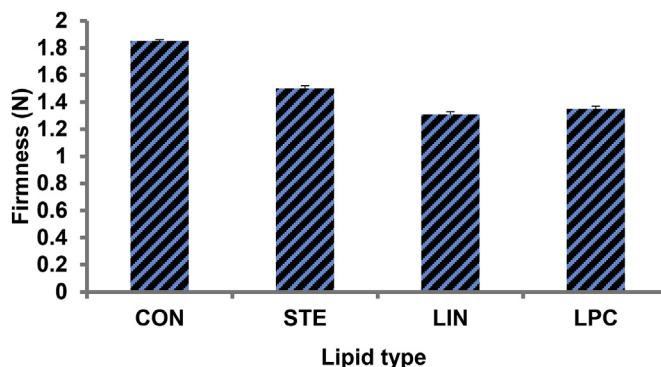


Fig. 3. Gel strength of Bambara groundnut starch gels with or without lipid at 2%. CON: Control, STE: Stearic acid, LIN: Linoleic acid, LPC: Lysophosphatidylcholine. Error bars indicate standard deviation (N = 3). Source: (Oyeyinka et al., 2016).

Bambara groundnut, corn and potato starches to differences in the chain length of amylose, this claim may require further validation. Previous studies similarly found that pulse starches, for example, cowpea starch, generally have higher DP than cereals and tuber starches (Chung et al., 1998; Won, Choi, Lim, Cho, & Lim, 2000). These authors associated the presence of longer amylose chains in cowpea starch to its higher gel strength and higher G' and G'' compared to maize and potato starches (Chung et al., 1998; Won et al., 2000).

3.3.2. Effect of lipids on thermal properties of Bambara groundnut starch

Thermal properties of starches modified with lipids has been widely studied using a DSC. Parameters such as the melting temperature (T_m) and melting enthalpy (ΔH_m) are important in assessing the degree of complexation of starch with lipids (Oyeyinka, 2017). The T_m allows for deductions to be made about the helical length of V-amylose complex, while ΔH_m provides information on the degree of order (crystallinity) in the complex and the amount of V-amylose complex formed (Kawai, Takato, Sasaki, & Kajiwar, 2012). One of the major limitations of native starch is their poor resistance to high temperatures usually encountered during processing. The interaction of lipids with various starches is known to improve starch thermal stability. Previous studies reported significant improvement in the thermal stability of Bambara groundnut starch after complexation with stearic acid, linoleic acid, lysophosphatidylcholine (Oyeyinka et al., 2016c) or with palmitic acid, stearic acid, oleic acid, linoleic acid (Oyeyinka et al., 2016b) and with lysophosphatidylcholine (Oyeyinka et al., 2016d). In general, Bambara groundnut starch complexed with different lipids reportedly displayed higher T_m values compared to the native starch (Oyeyinka et al., 2016b, 2016c, 2016d). The high T_m of V-amylose complexes is associated with the inclusion of the lipid in the amylose helix interior through hydrophobic interactions. According to Nimz, Gessler, Usón, Sheldrick, and Saenger (2004), these interactions are dominated by hydrogen-to-hydrogen van der Waals forces between hydrogen bonded to the 3rd and 5th carbons of glucose molecules with the hydrogen from the aliphatic chain of the lipid molecule. So far, studies on Bambara groundnut starch-lipid complexes have mainly produced Type I V-amylose complex with melting temperatures range between approximately 98 and 102 °C for starch-lipid complexes produced through pasting of Bambara groundnut starch with lipids (Oyeyinka et al., 2016c). Other report on starch-lipid complexes from Bambara groundnut starch formed using high pressure homogenization similarly reported melting temperatures (approx. 92 and 104 °C) corresponding to Type I V-amylose complex (Oyeyinka et al., 2016b, 2016d). However, homogenized complexes was found to produce more complex as shown by their higher ΔH_m values compared to the unhomogenized type (Oyeyinka et al., 2016b, 2016d). Compared to corn and potato starches, which are conventional source of starch for the industry, Bambara groundnut starch was reported to show higher complexing degree and higher thermal stability under the same experimental conditions (Oyeyinka et al., 2016b, 2016d). This was attributed to higher amylose content (31.5%) in Bambara groundnut starch compared to corn (22.5%) and potato (24.6%) starches (Oyeyinka et al., 2016b, 2016d). However, there studies where Type II complexes have been formed using corn starch. For instance, Type I or type II V-amylose complexes was reportedly formed when stearic acid was pasted with maize starch for short (approx. 12 min) and extended times (approx. 130 min) respectively (Obiro, Ray, & Emmambux, 2012). Variation in the thermal properties of starch-lipid complexes may be due to differences in amylose content as well as complexation conditions.

3.3.3. Effect of lipids on digestibility of Bambara groundnut starch

RDS of Bambara groundnut was found to significantly reduce by complexation with lipids (Oyeyinka et al., 2016c). The reduction (7–14%) was dependent on the type of lipid used (stearic, linoleic acid and lysophosphatidylcholine). Reduction in digestibility of complexed starches was attributed to the formation of amylose-lipid complexes (Oyeyinka et al., 2016c). According to these authors, the amylose-lipid interaction results in the formation of V-amylose single helical structure with a conformational hindrance that possibly restricts enzyme access into the starch granule interior. The reduced digestibility of Bambara groundnut starch after modification with lipids is beneficial and promising in the management of diabetes. Future studies may be required to incorporate the modified Bambara groundnut starch in food systems especially for formulating foods such as use as thickeners in yoghurt and cookies.

3.4. Application of modified Bambara groundnut starch

There is a growing demand for environmentally friendly materials such as edible bioplastics. Bio-based materials are promising renewable feedstocks that are theoretically recyclable and have a production process which is more energy efficient than petroleum-based plastics (Álvarez-Chávez, Edwards, Moure-Eraso, & Production, 2012). The most promising natural polymer that has been widely used in biodegradable film (BDF) production is starch. It has an attractive combination of availability, price, performance and good film-forming ability (Wilhelm, Sierakowski, Souza, & Wypych, 2003). The use of edible BDF in the food industry seems to be on the increase due to their wider application in extending the shelf life of foods by preventing changes in aroma, colour, texture, taste or handling characteristics (Tharanathan, 2003). Edible BDF made from native starches generally have poor mechanical properties, provide a minimal barrier to moisture and are very brittle. Modified Bambara groundnut starch has been reportedly used in biofilm application (Oyeyinka, Singh, & Amonsou, 2017). Bambara groundnut starch film was modified with stearic acid and show increased films solubility and opacity. According to these authors, Bambara groundnut starch films modified with stearic acid have improved thermal stability compared to unmodified starch films. Stearic acid (up to 2%) may be added to Bambara groundnut starch matrix for the preparation of biofilms with improved water vapour permeability and acceptable tensile strength. Future studies may require the use of the film in coating fruits and vegetables for extended shelf life. Additionally, modified Bambara groundnut starch may be employed as a low cost thickening agent for small and medium scale industry. This seems plausible since Bambara groundnut is currently a traditional crop grown mainly for subsistence. The cost of Bambara groundnut is much cheaper than corn and potato that are currently being used as a starch source for the industry. This may be one of several ways to increase income generation especially in developing nations of the world.

4. Summary and future research

Bambara groundnut represents a good and alternative source of starch for the industry. The higher melting temperature of the modified Bambara groundnut starch suggests that these starches would be useful in food that requires high-temperature processing such as in extruded products. Homogenized Bambara groundnut starch-lipid complexes may also be employed in the production of modified starch with non-gelling properties suitable for certain industrial application such as in frozen foods and desserts for better mouth feel. Future research is required to explore the unique non-gelling property of the homogenized Bambara groundnut starch-

lipid complexes in food systems. Furthermore, future studies should involve determination of amylose and amylopectin chain length distribution of Bambara groundnut starch as well as application of novel technologies and synergistic approaches in improving the functional properties of starch. For example, a combination of pulsed electric and lipid modification may be employed. Also, the use of sophisticated techniques such as the use of Nuclear magnetic resonance and Atomic force microscopy should be explored in future research.

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