Progress in research and applications of cassava flour and starch: a review

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Abstract The cassava flours and starches have elicited great use in the food and non-food industry. The diversity in cassava genotypes accounts for differences in end-product properties, and would require characterization of cassava varieties for suitability of culinary and processing. This review showed that screening criteria of cassava cultivars end-user properties include proximate contents, amylose content, structural, swelling, gelatinization and pasting characteristics, including freeze–thaw stability properties of cassava-derived flours and starches. Literature shows that the physicochemical properties vary with genetic factors (i.e. genotype). In this review, the amylose content was found to be the main genetic trait for discriminating the cassava varieties for gelatinization and pasting processes including resistant starches. Moreover, cassava derived raw materials (flours and starches) were found to have various application in baking, edible film, syrup, glucose, alcohol, and soups production.

Keywords Cassava starches · Bread · Edible film · Gelatinization · Pasting · Resistant starch

Introduction

Cassava (*Manihot esculenta* Crantz) is a staple food for over 800 million people in the tropics. It is cultivated over a wide variety of soils. Cassava ranks fourth among food staples with worldwide production of 276×10^6 t year⁻¹ (Uchechukwu-Agua et al. 2015). It is estimated to reach 290 million t year⁻¹ in 2020, and most of these will be expected to be cultivated in West Africa, tropical South America, and South East Asia (Uchechukwu-Agua et al. 2015; Zhu 2015). Among starch producing botanicals, including main cereal crops, cassava is the highest producer of carbohydrates per hectare and can be grown at considerably lower cost. Cassava is often viewed as ‘inferior crop’, ‘poor people crop’, and as ‘dangerous toxic crop’. These tags on cassava were due to some limitation of the crop including low quality and quantity of protein, and the presence of anti-nutritional factor cyanogenic glucosides that undermine its nutritional value.

Application of cassava flour and starch in product development and food formulations is guided by their end use properties such as composition, physicochemical and functional properties. Starch granules consist of two main types of glucans, amylose and amylopectin. Starch granules also consist of minor non-starchy components such as lipids, proteins and phosphates (Zhu 2015). The proportion, molecular weight, and chain length distribution of amylose and amylopectin glucans fundamentally influence the physicochemical properties of starches and starch based foods. The variation in composition and structures relate to the diversity in starch properties of different genotypic sources of cassava. The characterization of cassava starches is well documented. However, much research attention on physicochemical and functionality properties has been given to rice, wheat, barley, maize, and Irish potato

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starches. Thus, cereals and potato continue to dominate world markets for starches in food and non-food industries.

The breeding objectives for cassava have generated several varieties for increased yields, disease resistant, early bulking and improved human nutrition. There is an increasing industrial demand for starches with a global demand of 180 million t year⁻¹ (Jin et al. 2018) and considering the increased applicability of starch in food systems and non-food applications, different cheap and efficient alternative sources of starches with good physicochemical and functional properties should be explored. Cassava stands out among the underutilized starch sources because of its global availability, comparatively higher starch content and ease of extraction of its starch. The understanding of the properties of its starch is necessary to provide useful information on end use properties for product development and formulation. Documentation and catalogue of properties of technological importance will form a baseline of information to enhance selection of the most appropriate genotypes to meet the needs of cassava end-users such as farmers, breeders, and industry.

In this review, published research on the composition, structural, morphological, functional and physicochemical properties of cassava flour and starch are summarized, and gaps in knowledge identified. Application of gelatinization and pasting properties of the starch are reviewed and suggested. Further, data on digestibility of the resistant starch component of different cassava varieties were gathered.

Chemical composition and primary products of cassava

The cassava roots are deficient in protein and lipid contents. The shelf life stability of fresh cassava is limited due to rapid postharvest quality deterioration which occur immediately after harvest. High cyanides limits consumption of cassava.

Chemical composition of cassava varieties

The chemical composition is dependent on a number of factors such as cultivar, the geographical location, maturity stage of the plant, and environmental conditions (Mtunguja et al. 2016a). The proximate composition of cassava was reported (Table 1). Cassava is rich in carbohydrates and deficient in proteins and fats (Emmanuel et al. 2012). The protein contents of cassava are lower than those reported for potato (*Solanum tuberosum*) (Liang et al. 2019), Maize (*Zea mays*) (Ogunyemi et al. 2018) and wheat (*Triticum aestivum*) (Abdulrahman and Omoniyi 2016). Thus cassava has been described as nutritionally poor (Emmanuel et al.

2012). Efforts to increase its commercial utilization recognize blending cassava flour with other high protein content flours/starches derived from other botanical sources. Breeding objectives for increase nutritional quality in cassava has focused on bio-fortification of cassava with beta-carotene. The bio-fortified cassava is yellow fleshed and is the most recent genotype purposely bred to supply pro-vitamin A carotenoids in human diet (Uchekukwu-Agua et al. 2015).

Cassava primary products

The factors limiting utilization of fresh cassava include poor shelf life and high amounts of cyanides (Mtunguja et al. 2016a). Cassava fresh roots undergo rapid physiological postharvest deterioration (PPD) after harvest. The PPD reduces starch content resulting in poor functional properties. Because of PPD of cassava, it is essential to immediately transform fresh cassava roots into shelf-stable dried products. Processing of cassava roots leads to decreased cyanide content and improved shelf life stability. The cassava products are either fermented or unfermented (Uchekukwu-Agua et al. 2015) and contribute to the growing industrial application of cassava. The unfermented cassava primary products include flour and starch. The fresh cassava roots can be processed into chips, and the dried cassava chips can be transformed into flour or starch downstream.

Cassava starch

Starch is a polysaccharide produced in plants as a reserve of carbohydrates, and is commonly extracted by wet milling and filtration methods. The starch contents and yields are influenced by genotype. The amylose and amylopectin molecules are the major chemical constituents of starch granule.

Starch extraction

The common practice and primary method of extracting starch from fresh cassava is wet milling (Nand et al. 2008). Starch is extracted after wet milling through filtration, sedimentation, and decantation. Where centrifugation is used, a batch step of sedimentation is eliminated. The extracted wet starch is dried through sun drying, and oven drying at 35–40 °C for 12 h. Peeling of fresh roots before milling is a critical step. Cassava starch prepared from unpeeled or not properly peeled roots develop a grey color during wet storage, and purple color during drying (personal observations). The retained color lowers the quality thus affecting its value. Unfortunately, the extraction

Table 1 Proximate composition of cassava, corn, potato and wheat flours

Source	Moisture (%)	Ash (%)	Protein (%)	Lipid (%)	Fiber (%)	References
Cassava	33.14–45.86	-	1.76–3.48	0.74–1.49	1.38–3.20	Emmanuel et al. (2012)
Cassava	44.3–44.7	1.33–3.33	2.28–2.85	1.38–1.45	4.17–4.56	Oluwaniyi and Oladipo (2017)
Cassava	-	1.46–2.71	1.46–2.49	0.58–1.4	7.40–8.50	Rojas et al. (2007)
Corn	9.76–10.60	0.82–1.09	4.87–7.24	3.84–4.53	-	Ogunyemi et al. (2018)
Corn	8.66	1.23	7.28	5.22	4.69	Oluba and Oredokun-Lache (2018)
Potato	76.96–83.56	4.52–5.23	10.88–14.10	0.10–0.73	1.62–2.35	Liang et al. (2019)
Potato	76.1–81.00	4.50–5.00	2.9–10.60	0.15–0.65	1.50–4.90	Peña et al. (2015)
Wheat	11.82–12.2	0.36–0.38	10.65–11.50	0.82	-	Sameen et al. (2002)
Wheat	6.90	1.42	12.39	2.50	1.14	Abdulrahman and Omoniyi (2016)

Hyphen (-) implies value or information not found

methods are not standardized, to the extent that researchers applied different amount of water for extraction. For example a ratio of water to cassava slurry of approximately 2:1 was used by Abera and Rakshit (2003), while Nand et al. (2008) used ratio 10:1 of water to cassava slurry, respectively. In some reported methods, grating was conducted with sulphur-containing water for detoxification of toxic hydrocyanic acids (HCN) and also storing of fresh starch in sodium meta-bisulphite solution to inhibit the microbial growth.

Starch contents

Starch is the main constituent of cassava. Starch extraction yield expressed as fresh weight of peeled cassava and usually reported based on wet weight was in the range 17.28–35.37% (Schmitz et al. 2017). On dry weight, the starch yield from cassava root was estimated at 80% (Mejía-Agüero et al. 2012). Various factors affecting starch yield have been reported. Genotype and environmental conditions were mentioned to have influence on starch yield. However, genotype had significantly dominant effect. Mtunguja et al. (2016a) reported that genotype had huge influence on variability of starch contents and yields, while the effects due to variation in environmental factors were insignificant. Similarly, Mejía-Agüero et al. (2012) screened and compared starch content among twenty-five cassava cultivars planted and harvested simultaneously in a single plantation, and observed significant differences in starch contents due to inter-cultivar variability with insignificant influence from environmental factors. Therefore diversity of cassava genotypes accounts for differences in starch extraction rates (yields) and contents.

Composition of starch

The starch granule is a biopolymer of two major polysaccharides, namely amylose and amylopectin. These molecules consist of chains of α -(1-4)-linked D-glucose residues, which are interlinked with α -(1-6)-glycosidic linkages, thus creating branches in the polymers (Bertoft 2017). Amylose is the longer chains linear polymer composed of glucopyranose units, while amylopectin is the short chains branched polymer with significantly higher molecular weight (Singh et al. 2003). The amylopectin chains form double-helices responsible for the crystallinity in starch (Bertoft 2017). The semi-crystallinity in starch is due to the radially arranged linear and branched macromolecules (Singh et al. 2003).

The amylose content is the basis of classifying cassava starches into waxy, normal/regular and high-amylose types when amylose content is 0–15%, 20–35%, and higher than 40% of the total starch, respectively (Tester et al. 2004). Waxy cassava starch with zero amylose content was reported (Morante et al. 2016a) by weight. Most of the reported common cassava starches fell in the range of normal/regular starches (Table 2). High amylose starches were reported in corn varieties (Zhao et al. 2015; Liu et al. 2017), which implies that these corn varieties contained high content of amylopectin by weight, while wheat and potato were reported to be regular starches (Table 2).

The discrepancy in amylose content from different plants and within plant varieties could be attributed to varied starch isolation procedures used to determine amylose content (Zhu 2015). Previous research works have reported some of the common assay procedures for amylose content in starches, namely iodine-binding (Hernández-Fernández et al. 2016) and enzymatic method using Megazyme amylose-amylopectin assay kit (Nuwamanya et al. 2010b; Mtunguja et al. 2016b; Schmitz et al. 2017). The minor non-starch compounds in the starch granule

Table 2 Composition of cassava, corn, potato and wheat starches

Source of starch	Method	Amylose (%)	Ash (%)	Protein (%)	Lipid (%)	Phosphorus (%)	Fiber (%)	References
Cassava	Iodine-S	2.5–12	-	-	-	-	-	Mejía-Agüero et al. (2012)
Cassava	Starch assay procedure	21.0–22.5	0.36–0.37	0.13–0.17	0.37	-	0.20–0.23	Abioye et al. (2017)
Cassava	Iodine-S	19.25–32.12	-	-	-	-	-	Hernández-Fernández et al. (2016)
Cassava	K-AMYL	17.9–19.7	0.12–0.23	0.27	0.22	-	-	Nuwamanya et al. (2010b)
Cassava	K-AMYL	14.8–24.38	-	-	-	0.0034–0.0093	-	Schmitz et al. (2017)
Cassava	Iodine	0–20.3	-	-	-	-	-	Morante et al. (2016a)
Corn	Iodine	29.07–55.89	-	-	-	0.000–0.0013	-	Zhao et al. (2015), Singh et al. (2003)
Corn	Iodine	0.00–79.05	-	-	-	0.0076	-	Liu et al. (2017), Singh et al. (2010)
Potato	Iodine	24.1–31.9	-	-	-	0.0048	-	Cisneros et al. (2018), Singh et al. (2003)
Potato	Iodine	18.9–27.2	-	-	-	-	-	Ngobese and Workneh (2018)
Potato	Iodine	18.6–23.6	-	-	-	-	-	Frost et al. (2016)
Wheat	Iodine	6.2–20.9	-	-	-	-	-	Singh et al. (2017)
Wheat	Iodine	18.35–20.58	-	-	-	-	-	Karwasra et al. (2017)

Where *DSC* differential scanning calorimetry based method for amylose measurement, *K-AMYL* starch assay procedure of Megazyme, *Iodine-S* iodine-spectrophotometry/colorimetry based method. Hyphen (-) implies value or information not found

include protein, lipid, fiber and phosphorus, and are present in small percent by weight (Table 2) but can interfere in starch assay procedure. Lipids compete with iodine to bind amylose molecule to form complex (Singh et al. 2003). The complexes (amylose–lipid complex or amylose–iodine complex) may hinder actual estimation of amylose content. Boonpo and Kungwankunakorn (2017) reported that defatted cassava starch exhibited higher absorbance of amylose–iodine complex. Therefore, low non-starch and ash contents could potentially indicate high purity of extracted starches.

Amylose content can be suggested as basis for selecting flours/starches from different botanical sources for blending application. Starches with similar amylose contents can exhibit similar functionalities. However, variations in the structural properties; starch granule size and crystallinity, degree of polymerization, chain length of amylopectin structures (Table 3) would likely induce differences in starch functionalities.

Granular shape and size

Techniques for studying granular size and shape include scanning electron microscopy and light microscopy, while the granular surface features such as surface pores are investigated using atomic force microscopy (Zhu 2015). Common starches from different plants exhibited distinct

morphologies ranging from round, oval, truncated, lenticular or polygonal (Table 3). Oval, truncated shape was reported for cassava starch. Rice starches were reported to exhibit small granule sizes of sub-microns, while large granules sizes were found in potato starches. The variations in wheat starch granule sizes were ascribed to differences in genotype (Singh et al. 2010).

Crystallinity of cassava starches

As stated above, starch granule semi-crystalline nature contains crystalline and amorphous. The crystallinity is strongly associated with amylopectin molecule. Amylose is believed to be largely found in the amorphous lamellae and amylopectin forms crystalline lamellae (Zhu 2015). The structural crystallinity were identified as type A, B and C using X-ray diffraction analysis (Bertoft 2017). The A-type crystallinity are crystallites of double-helices of short chains, and are closely packed into a monoclinic unit cell containing 8 water molecules. The B-type crystallinity associated with crystallites of double-helices, which are loosely packed in hexagonal unit cell containing 36 water molecules. Some starches contain a mixed pattern (A and B) designated C-type (Bertoft 2017). The variation in double helices and packing pattern influences morphology and size of the starch granule (Singh et al. 2010). Cassava starches were reported to exhibit A- or C-type (Zhu 2015).

Table 3 Structural properties of commercial starches

Properties	Cassava ^{a,b,c,k}	Wheat ^{c,d,l}	Rice ^{c,e,f,l}	Corn ^{c,g,h,l}	Potato ^{c,i,l}
Shape	Oval, truncated	Round, lenticular	Polygonal	Round, polygonal	Round, oval
Diameter (μm)	2–30	2.7–28.5	0.8–8.7	5–20	5–100
Crystallinity type	A or C	A	A	A	B
Crystallinity (%)	25–34	28.2–36.5	-	-	-
A (> 15 μm) %	80	45.6–73.2	0–16.4	28.49–68.9	-
B (5–15 μm) %	20	14.0–37.0	47–72.5	26.13–63.78	-
C (< 5 μm) %	-	10.5–17.5	24.6–59.2	6.22–7.65	2.0–5.0
Amylose (M _w)	500–6000	980–1570	920–1110	-	4920–6340
Amylopectin (M _w)	3 × 10 ⁵ –3 × 10 ⁶	-	-	-	-
CL _n	16.1–22.8	17.7	16.9–18.1	19.7	23.1
DP < 13 (%)	35.9	44.5–52.4	30.1–34.2	12.4–22.7	9–9.1
DP 13–24 (%)	51.3	43.8–50.5	48.6–52.8	37.4–49.2	35–40
DP 25–36 (%)	11.3	3.7–6.5	9.5–9.7	13.4–15.6	13–14
DP > 36 (%)	1.5	-	7.5–7.6	13.3–34.6	38–43
Transmittance (%T)	57.1–69.6	28	24	31–46	96

DP_n degree of polymerization number, *GSD* (%vol) granule size distribution (percentage volume), *CL_n* amylopectin chain length, *M_w* size/molecular weight

^aBoonna et al. (2019), ^bZhu (2015), ^cBertoft (2017), ^dSingh et al. (2010), Polesi et al. (2016), Ramadoss et al. (2019), ^eSingh et al. (2006), ^hLin et al. (2016), ⁱSingh et al. (2008a), ^kMorante et al. (2016a), ^lSingh et al. (2003)

Other studies reported type B or C for cassava starch crystallinity. Conflicting results on cassava starch crystallinity polymorph type require careful examination. The crystallinity variations within plant varieties could be due to differences in water content. Liu et al. (2019) reported that crystallinity was influenced by moisture (water) content and heating conditions. The percent relative crystallinity varies among cassava varieties, it was higher in waxy than normal starch (Morante et al. 2016b).

Physical properties of cassava starches

The behavioral properties of starch in water include solubilization, swelling, gelatinization, and pasting. The paste clarity is characterized by light transmittance, while the cold storage behavior is characterized by freeze–thaw properties.

Swelling and solubility

Heating starch molecules in excess water results in disruption of crystalline structure and exposure of hydroxyl group. The formation of hydrogen bond by hydroxyl group and water molecules results in the swelling and solubility of starch granule. The past works reported swelling and solubility properties of starches from different sources in the temperature range of 50–95 °C (Table 4). Cassava and

wheat starches reportedly had the highest and lowest swelling power, respectively. Several factors were mentioned to be responsible for the variations in the swelling power of starches from different sources. Presence of non-starch components in the starch matrices was one of the most prominent factors reported. Variations in phosphorus content was adduced by Singh et al. (2003). The presence of non-starch compounds (lipids and proteins) were reported to have negative effect on swelling power. The protein compounds are known to restrict swelling of starch granules (Uthumporn et al. 2017) because of increased hydrophobicity which limits uptake of water (Muoki et al. 2015). Since cassava starch granule contain less lipids and protein than corn, wheat and potato starches, these could explain the highest swelling power and solubility values reported for cassava starch in the Table (Singh et al. 2003).

Furthermore, the differences in swelling power and solubility of starches were also linked to variation in amylose content. Mtunguja et al. (2016b) reported an inverse relationship between swelling power and amylose content in cassava starch. This was corroborated by Sánchez et al. (2010) who reported highest swelling powers (49.7–51 g/g) for waxy cassava starches. Singh et al. (2003) reported that starch granule swells as it absorbs water. Further swelling beyond a critical point results in the disintegration of the granule with subsequent release of soluble matters including amylose. This condition restricts further uptake of water thereby limiting swelling of the

Table 4 Swelling power (SP, g/g) and solubility (S, %) of cassava, corn, potato and wheat flours and starches

Starch source	Starch/ flour	Temperature (°C)									References
		SP/ S	50	60	70	75	80	85	90	95	
cassava	Starch	SP	-	-	8.9–12.3	-	-	-	13.5–16.3	-	Mtunguja et al. (2016b)
Cassava	Starch	SP	5.62–7.97	7.53–10.77	10.18–13.61	-	18.05–20.79	-	-	-	Nuwamanya et al (2010b)
Cassava	Starch	S	1.1–90.9	1.2–90.7	2.1–90.7	-	2.4–96.4	-	3.4–95.9	-	Demiate and Kotovicz (2011)
Cassava	Starch	SP	-	3.3	7.2	-	10.8	-	18.0	-	Chinma et al. (2013)
Cassava	Flour	SP	-	-	-	-	-	10.32–12.04	-	-	Eriksson et al. (2014a)
Cassava	Flour	S	-	-	-	-	-	10.98–20.77	-	-	Eriksson et al. (2014a)
Corn	Flour	SP	-	-	-	8.70–15.00					Moses and Olanrewaju (2018)
Corn	Flour	S	-	-	-	3.89–5.28					Moses and Olanrewaju (2018)
Corn	Starch	SP	-		-	-			15–30	-	Wang et al. (2017)
Corn	Starch	S	-	-	-	-			5–10	-	Wang et al. (2017)
Potato	Starch	SP	-	2.24	6.61	10.24	-	14.68	-	17.23	Verma et al. (2018)
Potato	Starch	S	-	0.29	3.24	7.65	-	9.21	-	11.10	Verma et al. (2018)
Potato	Starch	SP	-	3–5	5–10	10.15	-	10.15	-	30–35	Yadav et al. (2016)
Potato	Starch	S	-	5–7	5	5–10	-	25–30	-	10–15	Yadav et al. (2016)
Wheat	Starch	SP	-	4–6	6–8	8–10	-	9–10	-	10–12	Irani et al. (2017)
Wheat	starch	S	-	0.5–1	1–2	3–4	-	5	-	4	Irani et al. (2017)
Wheat	Flour	SP	1.83	2.36	4.26	5.44		-	7.38	-	Bashir et al. (2017)
Wheat	Flour	S	4.86	9.13	11.9	13.7		-	16.16	-	Bashir et al. (2017)

Hyphen (-) implies value or information not found

starch granule. However, presence of lipid which promotes formation of lipid-amylose complex could limit exudation of amylose (Singh et al. 2003).

Gelatinization properties

Gelatinization is an irreversible change that occurred when starch is heated in water. Its manifestation includes swelling, disruption of hydrogen bonds, crystallite melting with subsequent disappearance of Maltese cross, viscosity development, and starch molecules solubilisation when

heated in water. The transformation results in changes in viscosity and formation of a paste, which are influenced by the shape of starch granule, swelling power, and amylopectin/amylose ratio (Rolland-Sabaté et al. 2013). Gelatinization processes are characterized by the temperatures and enthalpies of the phase transitions and are determined using differential scanning calorimetry (DSC) (Zhu 2015).

Gelatinization is influenced by branch chain length of amylopectin (the branch chains are responsible for the double helical crystallites in starch granules). Transition temperature (T_p) of gelatinization was reported to be a

measure of crystallite quality (double helix length), while enthalpy of gelatinization (ΔH_{gel}) is an indicator of loss of molecular order within granule (Singh et al. 2003). Therefore, it follows that ΔH_{gel} correlates positively with crystallinity (Singh et al. 2010), and negatively with long chain amylopectin (Singh et al. 2010). Higher onset, peak and conclusion temperatures were reported for cereal and potato starches which contain high amount of lipids (Table 5). However, cassava starches exhibited lower onset gelatinization temperatures (Zhao and Saldaña 2019). The differences in gelatinization among different starches could be ascribed to variations in non-starch content, amylose content, amylopectin chain length, and crystallinity. The presence of amylose–lipid complex inhibits gelatinization of starch granules. Increased gelatinization temperatures resulting from increased amylose content were attributed to competing action between starch granule and amylose for water molecules (Lii et al. 1996). The presence of amylose–lipid complex inhibits gelatinization of starch granules (Charles et al. 2005). High levels of lipids were reported to lower starch granule susceptibility to gelatinization. Lipids may affect diffusion of water into the starch granules, and their presence on starch granules were demonstrated to retard gelatinization. Li et al. (2016) reported that defatted starch resulted in decreased gelatinization temperatures. The protein and starch granules compete for water molecules (Uthumporn et al. 2017) which probably results in inhibited swelling resulting in increased gelatinization temperatures. Amylopectin chain lengths were reported to influence gelatinization temperatures (T_o , T_p) as starches with high short amylopectin chain length (degree of polymerization less than 12) exhibited lower gelatinization temperature than long chain (Singh et al. 2006, 2010; Kaur et al. 2016). The failure in short chains to form double helical structures results in defect of crystalline nature, giving a granule a weak structure susceptible to disruption at low temperatures. Conversely, high gelatinization temperatures were associated with high degree of crystallinity (Singh et al. 2010), which relate to starch granule structural stability, and thus making it resistant to heating.

Retrogradation properties

Retrogradation takes place when amorphous starch molecules in aqueous medium (gelatinized starch paste) recrystallize to form double helical crystallites with accompanying loss of water-binding capacity. Starch retrogradation is accelerated by increasing the concentration of starch in the paste, increasing amylose content, increasing chain length of amylopectin and freeze-storage of starch paste (Wang et al. 2016). Amylose re-association is largely responsible for initial hardening of gel. The long

term gelling and retrogradation are mostly determined by amylopectin re-crystallization. The retrograded starch paste exhibit lower enthalpy and transition temperatures than native starch granule (Table 5). The transition temperatures are 15–20 °C and 7–10 °C, for cassava and wheat starch, respectively, lower than those for gelatinization of native starch granule. This trend was ascribed to weaker crystallinity of retrograded starch (Singh et al. 2003). The extent of decrease was higher in cassava starch than wheat, corn and potato starch paste. This could be ascribed to high tendency of cassava starch molecules to crystallise during cooling or cold storage. Furthermore, wheat contain higher proteins which accounts for improved emulsifying ability and facilitate protein–starch interactions resulting in high water-binding capacity. This has negating effect on recrystallization of starch molecules during the storage time (Wu et al. 2010). However, Zhao and Saldaña (2019) reported that pressurised hot water treatment of starch gave retrograded starch with higher transition temperature and enthalpy than native starches.

The differences in retrogradation is influenced by amount and type of starch crystallinity. The transition temperatures (T_o , T_p and T_c) of retrograded starch exhibit inverse and positive relationship with proportions of type A- and B-granules, respectively (Singh et al. 2010). This suggests that higher proportions of A-granules retrograded more than their B or C counterparts. Generally, the differences in thermal properties for starches between gelatinization and retrogradation are ascribed to variations in amylose content, non-starch content, size and shape of the granules (Singh et al. 2003).

Pasting properties

Pasting occurs after gelatinization, leading to the formation of amylose-amylopectin paste and gel network. Pasting properties are determined by rapid visco-analyser (Zhu 2015) or Brabender visco-amylograph. The pasting properties are investigated in terms of pasting temperatures, and viscosities which are characterized as peak, breakdown, and setback viscosities. The pasting properties of different starches are summarized in Table 6. The breakdown viscosity levels for cassava starches were generally half the peak viscosities, and similar trend was observed in some wheat, maize and potato starches. The Factors affecting pasting behavior are amylose contents and proportion of ingredients in the food system. Waxy cassava starches exhibited a narrow range of viscosities (Morante et al. 2016a) probably due to low amount of amylose contents. In a study on wheat starch, peak viscosity exhibited negative correlation with amylose content (Zeng et al. 1997). Cassava starches are associated with low pasting temperatures due to high levels of negatively charged phosphate groups

Table 5 Thermal properties of starches during gelatinization and retrogradation of cassava, wheat, rice, corn, potato and wheat starches

Starch	Gelatinization				Retrogradation				References
	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)	
Cassava	63.49–71.33	66.78–77.22	78.4–85.49	15.08–16.36	-	-	-	-	Charoenkul et al. (2011)
Cassava	63.9–69.1	68.9–75.5	80.3–85.6	14.2–16.2	48.5–52.1	54.7–59.7	61.6–65.1	1.3–2.0	Abera and Rakshit (2003)
Cassava	65.8	71.9	82.5	18.1	-	-	-	-	Hong et al. (2016)
Cassava	64.8	70.5	79.2	12.9	-	-	-	-	Zhang et al. (2013b)
Cassava	56.2–59.9	54.77–54.51	69.15–79.16	11.69–14.99	39.4–41.17	50.86–52.27	58.52–60.6	-	de Souza Fernandes et al. (2019)
Cassava	58.0–60.7	62.1–66.3	69.4–73	18.2–19.8	-	-	-	-	Morante et al. (2016a)
Cassava	64.1	69.9	79.5	14.9	-	-	-	-	Wongsagonsup et al. (2014)
Cassava	52.86–95.74	62.8–105.8	71.97–115.79	10.45–14.48	96.3–101.32	106.23–116.32	116.20–131.49	2.31–16.32	Zhao and Saldaña (2019)
Wheat	55.6–57.2	60.8–62.1	66.2–67.5	8.0–10.8	44.2–50.5	50.5–55.6	51.7–60.2	0.9–3.0	Singh et al. (2010)
Wheat	56.6	62.7	75.5	12.6	-	-	-	-	Irani et al. (2017)
Wheat	52.78–53.99	55.36–56.09	57.16–59.05	12.47–13.14	-	-	-	-	Kumar and Khatkar (2017)
Rice	60.8–71.8	65.7–75.9	72.2–82.4	4.0–5.1	-	-	-	-	Singh et al. (2007)
Rice	-	-	-	-	39.8	48.7	58.5	5.14	Wu et al. (2010)
Corn	60.5–68.4	67.8–73.5	76.1–81.3	6.4–17.6	-	-	-	-	Singh et al. (2006)
Corn	-	-	-	-	37.05–38.43	49.80–52.57	62.42–65.92	-	Singh et al. (2003)
Potato	55.4–59.6	58.8–62.4	65.2–68.1	5.0–8.0	-	-	-	-	Singh et al. (2008a)
Potato	-	-	-	-	59.72–60.70	63.26–64.58	67.28–70.34	6.42–8.61	Singh et al. (2003)

Hyphen (-) implies value or information not found, T_o onset temperature, T_p peak temperature, T_c conclusion temperature and ΔH is change in enthalpy of gelatinization

Table 6 Rheological and pasting properties of wheat, rice, corn and potato starches

Starch source	Viscoelastic		PT (°C)	Pasting			References
	Peak G' (Pa)	Peak G'' (Pa)		PV (RVU)	BV (RVU)	SV (RVU)	
Cassava	-	-	67.4–70	221–249	158–166	100–150	Charoenkul et al. (2011)
Cassava	60	30	71.9	238BU	142BU	89BU	Hong et al. (2016), Li et al. (2017)
Cassava	-	-	65.6	735	483	240	Zhang et al. (2013a)
Cassava	-	-	64.2–68.5	993–1149 cP	489–588 cP	277–531 cP	Morante et al. (2016b)
Cassava	471–1937	51.3–219	-	88.9–142.6	58.4–118.0	9.0–15.6	Charles et al. (2004)
Cassava	-	-	68.8	165	80.7	64.5	Wongsagonsep et al. (2014)
Wheat	6935	1370	82.3–87.2	2264–3433 cP	332–738	692–1673	Singh et al. (2003), Singh et al. (2010)
Wheat	-	-	82.1	2020 cP	464.5 cP	1619 cP	Irani et al. (2017)
Wheat	-	-	74.5–87.1	2193–3249 cP	342–728.5 cP	900–1445 cP	Kumar and Khatkar (2017)
Wheat	1310–8780	178–758	66.8–89.6	1010–3130 cP	664–1676 cP	572–3459 cP	Kaur et al. (2016)
Rice	20.63	1.101	-	728.7 cP	83.7 cP	510.3 cP	Chen et al. (2014)
Rice	6.4×10^3 – 1.6×10^4	1000–1700	-	-	-	-	Singh et al. (2007)
Corn	2000–17,000	450–2600	65.22–74.20	3096–4867 cP	1532–2898 cP	1414–2193 cP	Singh et al. (2006), (Wang et al. 2017)
Corn	6345	1208	66.3–69.0	804–1252	113–590	141–726	Singh et al. (2003), (Sandhu and Singh 2007)
Potato	8519	1580	66.2–68.7	4350–6800 cP	1500–4240 cP	238–436 cP	Singh et al. (2003), (2008a)

Hyphen (-) implies value or information not found, *BU* Brabender units, *PV* peak viscosity, *BD* breakdown viscosity, *SB* setback viscosity, *T_r* temperature range of the scanning program, *RVU* as viscosity unit, 1 RVU = 12 centipoise (cP)

in the cassava starch structures; viscosity development starts at lower temperatures. The higher contents of proteins and lipids, and subsequent formation of lipid-amylose complex could be the reason for higher pasting temperatures in cereal and potato starches. During cooling, the paste transforms into a gel. Cassava starches with low peak viscosities (1.6×10^3 – 2.3×10^3 cP) exhibited better culinary properties (cooking time, cooking loss and cooking weight) than starches with higher peak viscosity (2.3×10^3 – 2.8×10^3 cP) (Nuwamanya et al. 2010a).

Viscoelastic properties

The viscoelastic properties and effect of temperature on the behavior of the starch paste are significant rheological properties (Li et al. 2017). Brabender viscoamylograph and rapid viscoanalyser have been used extensively for measuring viscosity during heating and stirring of cassava starches. However, there is limited information on changes taking place in viscoelasticity of pastes from starch extracted from cassava. The dynamic moduli of rheometer allows for the measurement of flow behavior, viscoelastic and deformation characteristics as a function of applied stress during temperature and frequency sweep testing of the starch suspensions (Singh et al. 2003; Li et al. 2017).

According to Singh et al. (2003) the storage shear modulus (G') is a measure the energy stored in the material, while the loss shear modulus (G'') is a measure of the energy lost. The G' and G'' describes the elastic and viscosity of starch paste, respectively. The ratio of lost energy to stored energy is expressed as tangent ($\tan \delta$), which characterises the physical behavior of the system (Singh et al. 2003). The different starches exhibited larger storage modulus (G') than loss modulus (G'') (Table 6). The swelling of starch granules during heating leads to exudation of amylose molecules, which increases G' to the peak value. The increase in G' indicates formation of network of swollen granules in gel. However, as temperature increase beyond the peak value, G' decreases, suggesting rupture of swollen granule leading to destruction of gel structure. Faster destruction of gel structure are characteristic of sharper peaks, and broad peak showed slower destruction (Singh et al. 2006). Cassava starch exhibited smaller storage and loss moduli than other starches. The differences in viscoelastic properties were attributed to variations in granule structure, amylopectin chain length and amylose content. Starch granules with small size and oval shape showed smaller storage and loss moduli (Singh et al. 2003). Singh et al. (2008b) reported that legume (blackgram and pigeon pea) starch granules with high crystallinity levels exhibited

sharper peak and faster breakdown of gel structure than starches with low crystallinity levels.

Paste clarity of starch

The chemical components such as amylose and phosphorus may affect light transmittance of starch gels. Starch paste clarity was negatively related to amylose content. The waxy cassava starches were associated with high paste clarity and high swelling power (Morante et al. 2016a). Potato starch exhibited higher paste clarity than other starches (Table 3). The differences in paste clarity can be ascribed to higher presence of phosphorus, in the form of phosphate monoester, in potato starch (Singh et al. 2003). Phosphate monoester in starches from roots and tubers promote their hydrophilic nature, which increases paste transmittance and swelling power.

Resistant starches

The resistance of a starch material to digestion is associated to the extent of starch availability to enzymatic hydrolysis in the human digestive system. Resistant starch (RS) is a dietary fiber that does not get digested in the small intestine and has potential human health benefits. RS is influenced by the degree of gelatinization, and amylopectin branch chain length distribution (Abioye et al. 2017). Other factors affecting food RS content are amylose/amylopectin ratio, the degree of milling, heat applied under moist conditions, cooling, α -amylase inhibitors, and non-starch polysaccharides. There is limited information on RS content in cassava flour. Mejía-Agüero et al. (2012) reported high levels of RS in the range of 5.0–19.6% for cassava flour samples with characteristic C-type X-ray diffraction pattern, which are known to highly associated with slow or incomplete digestion in vitro and in vivo (Mejía-Agüero et al. 2012). Enzymatic susceptibility of cassava starches was due to amylose/amylopectin ratio, crystalline structure, and granular structure. Mejía-Agüero et al. (2012) also observed inverse relationship between RS and α -amylolysis index which was reported to be due to limited accessibility of amylase enzymes to RS zones in the starch granule. Similarly, (Mtunguja et al. 2016b) reported negative correlation coefficient between α -amylolysis and amylose content of cassava starch. This suggests that higher amylose starches would give higher resistant starch contents. The five types of RS were documented (Abioye et al. 2017). In the first type (RS I) starch is physically not accessible to enzymes and the breakdown of the granular structure is limited. The second type, (RS II), is ungelatinized granular starches with high crystalline levels as found in raw starchy foods such as unripe banana. The RS III type is produced following starch retrogradation. The other types, RS IV is due to chemical

modifications of starch, and type RS V is starch consisting of amylose–lipid complexes and characterized with high gelatinization temperatures and insoluble in water. The RS concept could be utilized as the basis of describing nutrition quality and potentially as criterion parameter for classification of cassava varieties.

Applications and utilization of cassava starches and flours

Starches and flours in the blend can influence each other's gelatinization and pasting properties. Commercial starches are derived from cereals, legumes, roots and tubers. Unfortunately, they are usually limited in certain desired properties and exhibit variation in pasting properties. However, starch from a known source may have unique properties that may determine its strength in some specific applications. For example, it was reported that cassava starch exhibited low cold paste viscosity (1800 mPa s) compared to potato starch (3400 mPa s) under similar conditions of 8% starch concentration and pasting temperature of 67 °C (Waterschoot et al. 2015). Mixing of different flours and starches can complement each other's functionalities to produce desired characteristics. Oladunmoye et al. (2014) reported that water-binding and absorption capacities increased with increased proportion inclusion of cassava starch into wheat starches. Inclusions of cassava flour and starch with other starches in food formulation can give rise to a wide range of properties to the finished product such as bread (Eriksson et al. 2014b). Amylose content and granule size of starch are important parameters in the behavior of starch blends. Some of the common application and uses of cassava flours and starches are blending of cassava flours/starches with other starches for edible films, soups, cream salads and alcohol productions.

Cassava–wheat composite flour for bread making

The inclusion of cassava flour into wheat in bread making is an important area towards the commercialization of cassava. Wheat based bread is widely consumed in many African countries and ranks third after maize and cassava in terms of supplying daily caloric intake. With increased wheat prices, there are challenges on the economic concern of vast importation of wheat grains. Thus, there is growing interest to promote the use of local sources of flour for partial substitution of wheat flour in bakery applications.

The unfermented cassava flour has been identified and is being promoted for this purpose. The cassava inclusion into wheat-based dough for bread making has been the subject of recent but limited investigations in various areas

pertaining to rheological properties and quality issues. The previous research efforts have concluded significant genotypic influence on physical, chemical and functional characteristics of cassava–wheat composite flour and bread quality. Baking properties of composite wheat–cassava flour with 10–30% cassava flour inclusion in the composite have been investigated (Eriksson et al. 2014b). It was found that the bread loaf quality varies according to cassava variety and percentage cassava flour inclusion into wheat flour (Eriksson et al. 2014b).

The leavening ability and cassava flour concentration were some of the quality parameters of research importance in the dough made from cassava–wheat composite flours on a cassava variety basis. However, there is limited information on associating physical parameters such as bulk density, water absorption capacity, and swelling power to pasting and rheological properties, and consequently on dough development, machinability (stickiness) and baking characteristics. In most part of literature, studies focused on associating cassava flour concentration with baking quality.

While cassava flour has been used in the formulation of cassava–wheat composite flours, the impact of freezing and frozen storage on cassava–wheat based bread dough is yet to be well investigated. However, related study on frozen storage of cassava starch showed that waxy cassava starch gel had no syneresis after 5 weeks of storage at -20°C and thus possessed the superior potential for formulating frozen or refrigerated foods (Sánchez et al. 2010).

Edible cassava films

The good paste clarity and gel stability including low gelatinization temperature of cassava starch make it an ingredient in formulation of food and biodegradable materials. The cassava starch films are documented as odorless, tasteless, colorless and non-toxin and have high paste clarity. Nevertheless, cassava starches are brittle with poor mechanical properties, but the incorporation of plasticizers reduces brittleness (Edhirej et al. 2017). Some of the common plasticizers of recent research focus in development of edible films are glycerol, urea, sorbitol, fructose, glucose and sucrose (Edhirej et al. 2017). Pinos-Hernandez et al. (2017), developed edible active films based on cassava starch, glycerol and natural polyphenols extracted from rosemary leaves. The inclusion of rosemary extract in glycerol-plasticized cassava starch films improved the UV-blocking properties of the films. Cassava films plasticized with 30% fructose gave better mechanical properties and showed reduced relative crystallinity from 0.31 to 0.21 (Edhirej et al. 2017). Cassava starch film with antioxidant and antimicrobial properties were developed by incorporating oregano essential oils and pumpkin residue

extract, and the film application on ground beef led to improved microbiological quality (Kechichian et al. 2010). The cassava starch-alginate coating/film incorporated with ascorbic acid was applied on pineapple fruits resulting in extended shelf life from 12 to 18 days at 23°C (Guimarães et al. 2017). The inclusion of granular cassava starch with nanosilver into konjac glucomannan (KGM)-chitosan films resulted in improved physicochemical properties. Specifically, the moisture barrier properties of (KGM)-chitosan films (Nair et al. 2017), and food contact tests exhibited reduced migration of silver that was significantly lower than the permitted level of migrating quantity of silver (10 mg/L) into stored bread samples, suggesting that KGM-chitosan-cassava starch-nanosilver films can be used as food-packaging materials.

The biodegradable film packages developed from cassava starch was tested for packaging bread. The packaging films were transparent, flexible and homogeneous and their surfaces were smooth, continuous and homogeneous, without pores, cracks or insoluble particles (Souza et al. 2012). The biodegradable cassava based film incorporated with natural anti-microbial components was also developed using casting techniques (Kechichian et al. 2010). Generally, the film performance of cassava starch is influenced by gelatinization technique and drying method (Flores et al. 2007). Excellent film forming properties of cassava starch further confirms the submission of Alcázar-Alay and Meireles (2015) that high amylose content starches are suitable for edible films.

Soups, sauces, salads and gravies

The call for increased dietary fiber intake in the general population has promoted production of fiber-enriched products. The white sauces have been functionalized to include dietary fiber such as resistant starches associated with reduced glycaemic index (Bortnowska et al. 2016). The native cassava starch was included at 2.5% level as an ingredient in recipe formulation of gluten-free white sauce. The inclusion stabilised the system resistant to phase separation (Bortnowska et al. 2016). Also, salad cream preparation containing cassava starch with pasting temperature $70.2\text{--}70.41^{\circ}\text{C}$ and final viscosity 3977 RVU was reported to exhibit acceptable sensory properties (Eke-Ejiofor 2015b).

Cassava alcohol and syrups

Glucose syrup processed from cassava starches was characterized and found to have 94.50–96.25% Dextrose Equivalent (DE), 0.13–0.20% total titratable acidity, 27.40°Brix sugar content and exhibited non-Newtonian behavior (Eke-Ejiofor 2015a), signifying potential properties for

production of commercial glucose syrup from cassava starches. Cassava starch was enzymatic treated by α -amylase from *Bacillus licheniformis* and glucoamylase from *Aspergillus niger*, and the resulting glucose syrup producing alcohol (ethanol) was characterized with productivity of $1.8\text{--}3.2\text{ g L}^{-1}\text{ h}^{-1}$ (Ruiz et al. 2011). The yields of 98% glucose syrup and 42% fructose syrup of cassava starches were achieved in 24 h and 96 h, respectively following enzymatic hydrolysis by *Aspergillus niger* and *Streptomyces* sp (Silva et al. 2010). High yields of alcohol 8.72% (v/v) were formed from cassava flour (Ocloo and Ayernor 2010).

Discussion

The breeding objectives of cassava have led to increased cassava varieties with the focus on increased yields, human nutrition, and disease tolerance. The introduction and the official release of new improved cassava varieties would require screening for suitability of processing and culinary usage. The cassava flours and starches were characterized in terms of amylose content, swelling, solubility, gelatinization, retrogradation, enzymatic susceptibility and pasting. The factors affecting swelling and solubility were in most part of the literature limited to amylose and particle/granule size. There is a need to investigate swelling and solubility of cassava flours and starches as the function of bulk density, porosity and compressibility. Characterization of cassava starches in terms of their molecular weight, amylose and amylopectin chain lengths linking toward the end functional properties for newly developed cultivars deserve to be studied.

The information on the investigation of amylose and amylopectin ratio effect on swelling, solubility, gelatinization, retrogradation, enzymatic susceptibility and pasting were limited to native cassava starch. There is a need to analyze the amylose and amylopectin ratio of the cassava varieties and consequently investigating the effect of amylose and amylopectin ratio on the physicochemical properties of starches and cassava utilization end products. In the most part of the literature, limited studies on non-starch contents such as phosphorus, lipids and proteins have been their influence cassava starch properties. The gap is that the non-starch components were not analyzed in most of the reported cassava cultivars. Consequently, the influence of these components on swelling, solubility, gelatinization, retrogradation, enzymatic susceptibility and pasting properties cannot be properly ascertained. The non-starch contents of the new cassava cultivars deserve to be studied.

Studies on composite flours of cassava–wheat for bread making have investigated rheological properties and baking characteristics on the variety basis. However, from the

market side, cassava flours are usually a composition of flours from various cassava cultivars. Standardization is imperative for pricing and uniformity of quality of final baked products. There is a need to optimize rheological and pasting properties of different cassava flours and starches to obtain optimized blend of cassava flours/starches which can be added to wheat. Furthermore, there is a need to incorporate extracted cassava starch into blends and to investigate the effect it has on pasting properties and bread quality. The inclusion of starches in gel forms would require testing. These forms could impact different rheological properties of the dough and subsequently on the baking characteristics. The waxy cassava starch gel had no syneresis after 5 weeks of storage at $-20\text{ }^{\circ}\text{C}$ (Sánchez et al. 2010) and thus possessed the superior potential for formulating frozen or refrigerated foods. One such food formulation could be the incorporation of cassava flour in the frozen wheat dough for bread making. The performance of selected cassava flours/starches deserves to be investigated in frozen wheat dough for bread making.

Studies profiling assimilation of active ingredients such as surfactants, antioxidants, oils and vitamins on cassava starch gels are yet to be investigated. Nevertheless, the physicochemical properties and functionality of cassava starches have found use in various industrial applications including production of edible films. The composite flours made from cassava flour and wheat has elicited great use in bakery industry. Depending on gelatinization and pasting profiles, cassava starches can be used in production of soups, salad creams, and gravies. The cassava starches and flours have been used in production of alcohols, glucose and fructose syrups targeted for food and beverage industries. For the non-food industry, bio-ethanol fuel production from cassava is common, and is well researched in Thailand, Vietnam, and Brazil. However, in Africa, the industrial consumption of cassava starches is yet to be scaled-up, and therefore there is a need for increased research inclined towards screening of cassava flours and starches to ascertain suitable industrial applications.

Conclusion

The physicochemical and structural properties are principal selection criteria of cassava flours and starches for use in the food industry. The properties such as swelling, solubility, gelatinization, pasting, retrogradation, enzymatic susceptibility are genetic factor dependent. Besides genetic factors, the amylose and amylopectin ratio, granular size and shape are some of the factors for investigation of swelling, solubility, gelatinization, pasting, enzymatic susceptibility and retrogradation properties of cassava flours and starches.

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