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Physicochemical properties of chemically modified starches from selected improved cassava species

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Abstract

Starches obtained from five selected improved cassava species (NR 93/0199, TMS 96/0304, TMS 98/0581, TMS 92/0326, TMS 98/12123) were chemically modified by oxidation, acetylation and acid-thinning. Physicochemical properties of these starches were investigated for applications in a variety of industries. Acetylated starches significantly ($p<0.05$) gave the highest values in: least gelation concentration (11.20%), swelling power (31.07 %), water absorption capacity (67.00 %), oil absorption capacity (85.60 %), viscosity (101.180 mPas), specific volume (10.25 ml/g) and lowest in starch solubility (21.51 %). Acid-thinned starches significantly ($p<0.05$) yielded the lowest values in least gelation concentration (6.80 %), oil absorption capacity (68.20 %), viscosity (98.17 mPas), specific volume (2.92 ml/g) and highest value in blue value index (2.63 %). Oxidized starches had the lowest value of 14.27 % in swelling power. TMS 96/0304 significantly ($p<0.05$) had the highest values in swelling power (24.47 %), blue value index (2.79 %) and lowest value in specific volume (5.54 ml/g). Highest values were obtained in specific volume (6.82 ml/g) for NR 93/0199 and in viscosity (101.88 mPas) for TMS 98/12123 among the cassava species. These results obtained highlighted the potentials of these starches in the manufacture of confectioneries, salad cream, mayonnaise, texturizing agents, thickeners, stabilizers, fillers, flavouring agents, beverage and bakery products.

Keywords: improved cassava species, native and chemically modified cassava starches, oxidation, acetylation, acid thinning, physicochemical properties and applications

Introduction

Starch as one of the most abundant substances in nature, renewal and almost unlimited resource (IITA, 2005; Iwe *et al*., 2014) [13, 15], is currently receiving increased attention owing to its wide usefulness in different food and non-food applications. Pure starch is a white, tasteless and odourless powder that is insoluble in cold water or alcohol (BeMiller and Whistler, 2009; Okereke, 2012; Okereke *et al*., 2021) [3, 29, 30]. It consists of two types of molecules- the linear helical amylose, and branched amylopectin; and they play key roles in determining the physicochemical properties of starches (Nuwamanya *et al*., 2011; Okereke *et al*., 2021) [30]. Depending on the plant, starch generally contains 20 - 25% amylose and 75-80% amylopectin (Ihekoronye and Ngoddy, 1985; Gotlieb and Capelle, 2005; Okereke *et al*., 2021) [30].

Starch (a polymer of glucose molecules) is the most important human diet and is contained in such staple foods as potatoes, sweet potatoes, arrowroots, wheat, cocoyam, yam, maize, rice and cassava (Lawal, 2004; Okereke *et al*., 2021) [21, 30]. Cassava is an important food crop in the tropics – a major carbohydrate staple food consumed in various forms by humans (Hassan, 2011) [9]. Its usage as a source of ethanol, roughage, biofuel, energy in animal feed and starch for industry is increasing. Presently, Nigeria produces a large tonnage of cassava and it is ranked the highest producing nation (Ukpabi *et al*., 2004; Babaleye, 2007; Okereke *et al*., 2012) [39, 2, 3]. Nigeria stands out as a country in Africa that has witnessed full and genuine Presidential support for promotion of cassava starch (Babaleye, 2007; Hassan, 2011) [2, 9]. Therefore, the huge domestic and industrial potentials of cassava need to be fully exploited since it represents a valuable subsistence and cash crop in many countries. Advantages of cassava starch are high level of purity, excellent thickening characteristics, neutral (bland) taste, desirable textural characteristics, relative cheap source of raw material that can surpass the properties offered by other starches from wheat, maize, potatoes and rice (Iwe *et al*., 2014) [15]. Cassava starch is easy to extract using a simple process with limited capital and it is often preferred in adhesive production as these adhesives are viscous, work more smoothly and provide stable glues of neutral pH (Okereke, 2012) [29].

Native or unmodified starches have limited usage (Ihekoronye and Ngoddy, 1985) due to their inherent weakness of hydration, swelling and structural organization (Okereke, 2012; Iwe *et al*., 2014) [29, 15]. To enhance viscosity, texture and stability among many food and non-food industrial applications, starches and their derivatives are modified by chemically, physically and biotechnologically means (Okereke, 2012; Okereke *et al*., 2021) [29]. Starch modification aims at correcting the inherent detrimental properties of native starches and

thereby introducing specific functionalities. Food processors prefer starches with better behavioural characteristics than those provided by native starches (Miyazaki *et al.*, 2006).
Modified starches are prepared by physically, chemically or enzymatically treating native starches thereby changing properties of the starches. Starches may be modified to increase their stability against excessive heat, acid, shear time cooling or freezing; to change their texture; to decrease or increase their viscosity; to lengthen or shorten gelatinization time or increase their visco-stability (Miyazaki, 2006; Okereke *et al*., 2021).
Modified starches are used, in practically all starch applications such as in food products as a thickening agent, stabilizer or emulsifier; in pharmaceuticals as a disintegrant or in paper and textiles as a binder (Okereke *et al*., 2012). They can also be used as stiffening or gluing agent or processed to produce sugars in processed foods. Widely used prepared foods containing modified starches are bread, pancakes, beverages, flavouring agents, cakes, cereals, noodle, pasta, porridge and tortilla (Hassan, 2011; Okereke, 2012; Iwe *et al*., 2014) [9, 29, 15,]. According to Ibe (2010), developing cassava starches with good physico- chemical and baking potentials will help to realize the vision of expendable utilization of cassava in Nigeria, promoting food security, increasing employment and contributing to economic growth.
Grown over a wide range of soil profile, many species of cassava that are disease and drought resistant have been developed (Kulakow, 2009). For example, many improved cassava cultivars with relatively high dry matter and starch contents have been developed in Nigeria by National Root Crops Research Institute (NRCRI) Umudike and International Institute of Tropical Agriculture (IITA) Ibadan (Ukpabi *et al*., 2004; Babaleye, 2007; Ogala, 2010) [39, 2]. Equally important is the need to undertake strategic research to identify, develop and promote cassava species that can meet the standards of starch-based industries for high quality starches at affordable prices. In this vein, continuous studies are being promoted to reveal other potentials of these species for efficient utilization and application in the industrial sector. Thus in view of this, chemical modification of starches from five available improved cassava species (NR 93/0199,TMS 98/0581, TMS 96/0304, TMS 92/0326 and TMS 98/12123) using acetylation, oxidation and acid- thinning methods in order to investigate their physicochemical and functional properties will be the focus of this study.

Materials and Methods

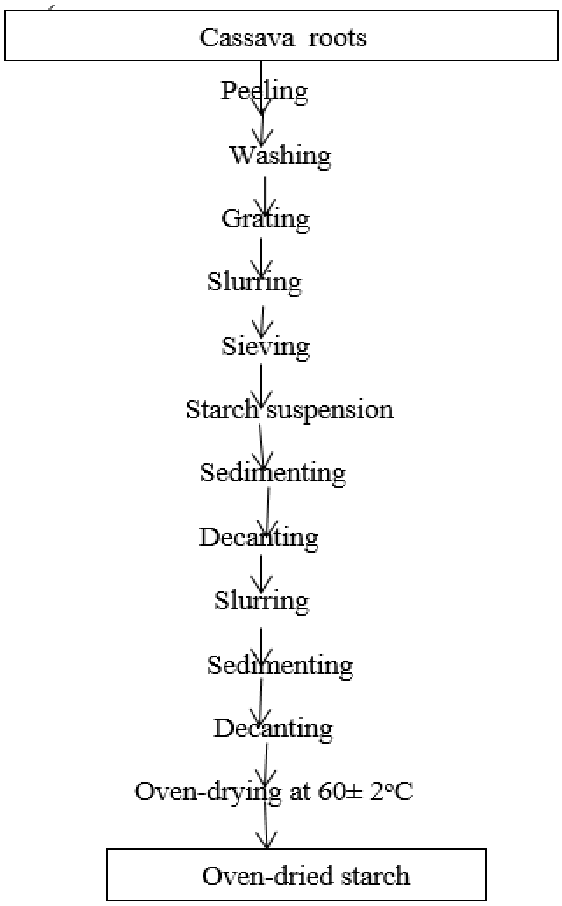
Materials

Fresh tubers from five improved (disease – resistant and high starch content) cassava species were obtained from Cassava Programme of the National Root Crop Research Institute (NRCRI) Umudike, Nigeria. The cassava species were NR 92/0199, TMS 98/0581, TMS 96/0304, TMS 92/0326 and TMS 92/12123.

Methods

Starch extraction

Starch was extracted from cleaned, peeled and macerated cassava roots using the method of Kaur *et al*., (2016).



Modification of the Starches

Portion of oven dried starch (i.e at 60± 2°C) from each of the selected improved cassava species was chemically modified through acetylation, oxidation and acid – thinning processes. For acetylation, the method of Sathe and Salunkhe (1981) [33] was used. The method of Forssel *et al*. (1995) was adopted for oxidation, while the method described by Lawal (2004) [21] was employed for acid-thinning.

Determination of the Physicochemical Properties

Swelling power

Swelling index of starch samples were determined using the method described by Ukpabi and Ndimele (1990) [38].

Water Absorption Capacity

The method of Sosulski (1962) [35] was used to determine the water absorption capacity of the starch samples.

Oil Absorption Capacity

It was determined by the method of Sosulski (1962) [35].

Blue Value Index

Blue value index indicates the extent of the breakdown of the starch molecules in the native starches (Abbey and Ibe, 1988).

Solubility

The cold water extraction as described by Udensi and Onuora (1992) was employed.

Gelation Capacity

Gelation capacity was determined according to the method of Coffman and Garcia (1977).

Viscosity Test
The method of Onwuka (2005) was employed.

Experimental design
The experiments were fit into two-way ANOVA/classical model of 4 x 5 factorial designs and the resultant of any variation due to main effect and their interaction were established. The main effects included modification methods (4) and selected cassava species (5).

Statistical analysis
Analyses were done in triplicates. Data obtained from the analyses were subjected to analysis by variance (Ihekoronye and Ngoddy, 1985; Iwe, 2002). Fishers LSD (p<0.05) were used to separate the means that have significant difference (Iwe, 2002).

Results and Discussion

Table 1: Swelling Power (%) of Cassava Starches as affected by modification methods and Cassava species

	Chemical Modification Method					
Cassava Specie	Native	Oxidation	Acetylation	Acid-thinning	Mean±SD	LSD
NR 93/0199	21.73	15.78	29.46	14.76	20.43 ± 6.76^{ab}	5.19
TMS 96/0304	25.93	15.78	33.93	22.22	24.47 ± 7.58^{a}	5.19
TMS 98/0581	25.93	12.30	34.92	17.47	22.66 ± 9.92^{ab}	5.19
TMS 92/0326	21.99	15.78	27.60	12.70	19.52 ± 6.63^{ab}	5.19
TMS 98/12123	17.26	11.71	29.46	13.10	17.88 ± 8.07^{b}	5.19
Mean±SD	28.21 ± 3.60^{a}	14.27 ± 2.08^{b}	31.07 ± 3.17^{a}	16.05 ± 3.93^{b}		
LSD	4.33	4.33	4.33	4.33		

***** Results are the means of triplicate samples ± SD
* Means with different superscripts differ significantly at $p < 0.05$
* LSD means least significant difference

Effect of Cassava Species and Modification Methods on Swelling Index (%) of the Cassava Starches
Results of the effects of chemical modification methods (oxidation, acetylation and acid-thinning) and cassava species (NR 93/0199, TMS 98/0581, TMS 96/0304, TMS 92/0326, TMS 98/12123) on the swelling power of the cassava starches are presented in Table I. Swelling capacities of the starches are dependent on the modification processes and species of the cassava.
The results show that modification of starches using acetylation method increased the swelling power (31.07%) of the native starches, while acid-thinning and oxidation methods decreased the swelling power significantly to values of 16.05% and 14.27% respectively. This result agrees with the earlier reports on acetylated starches (Desphande *et al.*, 1982; Lawal, 2004; Yusuf *et al.*, 2007; Ibe, 2010) [6, 21, 42]. According to Lawal (2004) [21], acetylation reduces intermolecular association in the starch granules and this reduces structural limitations against swelling. Acid thinning treatment increases percentage relative crystallinity and this accounts for the reduction of the swelling capacity as swelling is restricted by stiffness of the entangled amylopectin network in the crystalline region of the starch (Ikegwu *et al.,* 2010) [12]. The reduction in swelling after oxidation is attributed to structural disintegration within the granules of the starch as the oxidizing agents penetrate deeply into the granule acting mainly on the amorphous regions (Lawal, 2004; Gotlieb and Capella, 2005) [21]. Acid thinning reduces the molecular weight of the amylose and amylopectin backbones within the granule without disrupting the integrity of the granule itself.
Species of the cassava affected significantly ($p < 0.05$) the swelling capacity of the starch with TMS96/0304 recording highest value (24.47%) and TMS98/12123 producing the least value (17.88%). This indicates that specie of cassava is a critical factor in swelling power of cassava starch and affects the amylose and amylopectin content of the starch. Thus it further suggests that species with low values contain higher amylose content and thus have lower swelling capacities and smaller gel strength (Moorthy, 2002; Bemiller and Whistler, 2009) [3]. This is in agreement with the report of Tester and Morison (1990) [36] that swelling behaviour is the property of its amylopectin and amylose contents where amylose acts as a diluent and inhibitor of swelling. This agrees also with other reports which stated that the packing of amylose and amylopectin within the granules vary among starches from different species (Nunez-Santiago *et al.,* 2004; Uzomah and Ibe 2011) [26, 40]. These differences in swelling power values of various starches were largely attributed to different intensities of molecular association forces inside the granules and these factors are governed by factors which include amylose and amylopectin contents and ratio, molecular weight, conformation, polymerization degree of both fractions, degree of branching of amylopectin and the effect of different modification treatments on the structure of the starch (Shimellis *et al.,* 2006; Ikegwu *et al.,* 2010) [12]. In some instances the amylose chain contributes effectively to maintaining the granule integrity by complexing with lipids and facilitating the linkage among amylopectin chains. The amylose content of the starch granules varies with the botanical source of the starch and is affected by the climatic conditions and soil type during growth (Morison and Azudin, 1987; Chanvrier *et al.,* 2007) [23]. From the results obtained, starches of TMS 96/0304 source and acetylated one are preferred in food systems where high swelling ability would be needed to control volume or size (Uzomah and Ibe 2011) [40]. Swelling power is an indication of the water absorption index of the granules during heating (Ikegwu *et al.,* 2010) [12]. It reflects the extent of the associative forces within the granule.

Table 2: Solubility (%) of Cassava Starches as affected by modification methods and cassava species

	Chemical Modification Method					
Cassava Specie	**Native**	**Oxidation**	**Acetylation**	**Acid-thinning**	**Mean±SD**	**LSD**
NR 93/0199	28.30	35.63	22.56	36.07	30.64± 6.64[ab]	0.90
TMS 96/0304	26.47	33.77	21.33	33.63	28.80 ± 6.04[c]	0.90
TMS 98/0581	24.07	31.40	19.27	31.20	26.49 ± 5.90[c]	0.90
TMS 92/0326	27.10	35.10	21.70	35.23	29.78 ± 6.60[b]	0.90
TMS 98/12123	28.13	35.27	22.67	36.37	30.86 ± 6.69 [a]	0.90
Mean±SD	26.81±1.71[b]	34.43 ± 1.92[a]	21.51±1.37 [c]	34.50 ± 2.13[a]		
LSD	0.71	0.71	0.71	0.71		

* Results are the means of triplicate samples ± SD
* Means with different superscripts differ significantly at $p < 0.05$
* LSD means least significant difference

Effects of Cassava Species and Chemical Modification Methods on the Solubility of the Cassava Starches

Results of effects of cassava species and chemical modification methods on the solubility of the cassava starches are presented in Table 2. Acid thinned cassava starch had the highest solubility index (34.50%) though not significantly different ($p < 0.05$) from oxidized starch (34.43%) while acetylated starch had the least solubility (21.51%). Both acid thinning and oxidation significantly ($p < 0.05$) improved the solubility of the native starches. On the other hand, acetylation led to significant ($p < 0.05$) reduction of solubility of the native starch (Lawal, 2004; Uzomah and Ibe, 2011) [21] from 26.8% to 21.5%. In a study of the solubility pattern of various starches, it was found that 60 – fluidity acid-modified corn starch was about four times as soluble as its parent starch in water at 85^0C. There was also a report of increase in solubility of cornstarch at all temperatures following oxidation (Sandhu and Singh *et al*,, 2007; BeMiller and Whistler, 2009) [32, 3]. Acid modification improved solubility of cassava starch (Lawal, 2004) [21] and red bean starch (Kim and Ahn, 1996; Yusuf *et al.*, 2007) [19, 42].

In acid-modification, the hydroxonium ion (H_30^+) attacks the glycosidic oxygen atom and hydrolyzes the glycosidic linkage. Acid acts on the surface of the starch granule first, before it gradually enters the inner region (Lawal, 2004) [21]. Then, the acid preferentially attacks the amorphous regions because the crystalline area is not freely accessible to the acid and this allows it to remain intact.

Cassava species significantly ($p < 0.05$) affected the solubility of the cassava starches. TMS 98/0581 had the least solubility (24.49%), which was not significantly ($p > 0.05$) different from TMS 96/0304 (28.80%) while TMS 98/12123 had the highest solubility (30.86%) which differed insignificantly ($p > 0.05$) from NR 93/0199 (30.64%). This indicates that specie of cassava significantly ($p < 0.05$) affects solubility of starches. This difference could be attributed to differences in amylose and amylopectin ratio, granule size, molecular weights and presence of naturally occurring impurities of non-carbohydrate nature (Lawal, 2004) [21].

Table 3: Water Absorption Capacity (%) of Cassava Starches as affected by modification methods and cassava species

	Chemical Modification Method				
Cassava Specie	Native	Oxidation	Acetylation	Acid-thinning	Mean±SD
NR 93/0199	56.67	53.33	66.67	36.67	53.34 ± 12.47
TMS 96/0304	53.33	50.00	63.33	33.33	50.00 ± 12.47
TMS 98/0581	48.33	53.33	75.00	36.67	53.33 ± 16.04
TMS 92/0326	56.67	53.33	63.33	41.67	53.75 ± 9.06
TMS 98/12123	40.00	56.67	66.67	48.33	52.92 ± 11.42
Mean±SD	51.00± 7.03[b]	53.33± 2.36[b]	67.00 ± 4.77[a]	39.33 ± 5.84[c]	
LSD	11.00	11.00	11.00	11.00	

* Results are the means of triplicate samples ± SD
* Means with different superscripts differ significantly at $p < 0.05$
* LSD means least significant difference

Effects of Chemical Modification Methods and Cassava Species on the Water Absorption Capacity of the Cassava Starches

The effects of chemical modification methods and cassava species on the water absorption capacity of cassava starches are shown in Table 3. The results show that hydrophilic tendency of the starches improved after oxidation and acetylation whereas acid-thinning reduced the tendency of the starch to absorb water. The highest value of 67.00% was observed for acetylated starches against 53.33% and 51.00% recorded for oxidized starches and native starches respectively. Acid-thinned starches showed a lower value of 39.33% than did native starches indicating impairment of hydrophilic properties of the native starches after acid-thinning modification. These results were less compared to previous observation by Sosulski (1962) [35] who reported $2.99gg^{-1}$ water absorption capacity for Great Northern bean starch. This different behaviour after modification of the starch could be attributed to the difference in amylose/amylopectin ratio, as well as to the difference in chain length distribution (Ikegwu *et al.*, 2010) [12]. According to Ikegwu *et al.*, (2010) [12], water binding capacity of starches is a function of several parameters including size, shape, conformational characteristics, steric factors, lipids and carbohydrates associated with proteins and others. Acid-thinning basically reduced water absorption capacities because of reduction of the amorphous region in the starch granules. Therefore, this reduced the number of available binding sites for water in the starch granules. However, cassava species had no significant (p <

0.05) effect on the water absorption capacity of the cassava starch. The result obtained is in agreement with the report of Lawal (2004) [21] and contrary to that of Sathe and Salunkhe (1981) [33] in which acetylation and oxidation did not improve water absorption capacity of Great Northern bean starch.

The report of Desphande *et al.* (1982) [6] in which acetylation and oxidation improved the oil and water absorption capacities of black grain starch by almost 2.5 time more than that of the control strengthens this result.

Ikegwu *et al.,* (2010) [12] reported that the ability of food to absorb water and oil may help to enhance sensory properties such as flavor retention and mouth-feel. This imbibition of water is an important functional trait in foods such as sausages, custards and doughs. This implies that acetylated starches will have a higher degree of flavor retention and mouth-feel than the other starches. Cassava species have no significant effect on the water absorption capacity of the cassava starches

Table 4: Oil Absorption Capacity (%) of Cassava Starches as affected by modification methods and cassava species

Chemical Modification Method					
Cassava Specie	**Native**	**Oxidation**	**Acetylation**	**Acid-thinning**	**Mean ±SD**
NR 93/0199	76.00	80.67	83.00	70.00	77.42 ± 5.74
TMS 96/0304	73.00	79.00	88.00	67.00	76.75 ± 8.96
TMS 98/0581	76.00	79.00	88.00	67.00	77.50 ± 8.66
TMS 92/0326	76.00	80.67	85.33	67.00	77.25 ± 7.82
TMS 98/12123	77.67	79.00	83.67	70.00	77.59 ± 5.67
Mean±SD	75.73 ± 1.69^{c}	79.67 ± 0.92^{b}	85.60 ± 2.35^{a}	68.20 ± 1.64^{d}	
LSD	3.65	3.65	3.65	3.65	

* Results are the means of triplicate samples ± SD
* Means with different superscripts differ significantly at $p < 0.05$
* LSD means least significant difference

Effects of Chemical Modification Methods and Cassava Species on the Oil Absorption Capacity of the Cassava Starches

Table 4 shows the effects of chemical modification methods and cassava species on the oil absorption capacity of cassava starches. The results show that hydrophobic tendency of the starches improved after oxidation and acetylation whereas acid-thinning reduced the tendency of the starches to absorb oil (Lawal, 2004; Uzomah and Ibe, 2011) [21]. The highest value of 85.60% was observed for acetylated starch against 79.67% and 75.73% recorded for oxidized and native starches respectively. Acid-thinned starch showed the least value of 68.20% indicating impairment of hydrophobic capacity of the starch after acid thinning process. Acetylation and oxidation improved the oil absorption capacity of black grain starch by almost 2.5 times more than the control (Desphande *et al.,* 1982) [6], contrary to the report of Sathe and Salunkhe (1981) in which acetylation and oxidation did not improve oil absorption capacity of great northern bean starch. Improvement in oil absorption is a result of introduction of functional groups on the starch molecules which facilitate a more enhanced, binding capacity than the native starch (Lawal, 2004; Uzomah and Ibe, 2011) [21]. Acid-thinning basically reduced oil absorption capacity because of reduction of the amorphous region in the starch granules. This reduces the number of available binding sites for oil in the starch granule (Yusuf *et al.,* 2007) [42].

However, specie of cassava had no significant ($p < 0.05$) effect on the oil absorption capacity (Uzomah and Ibe, 2011) [40]. Moreover, oil absorption capacity is useful in structure interaction in food especially in flavour retention and improvement of palatability and extension of shelf life particularly in bakery or meat products (Gotlieb and Capelle, 2005; Ikegwu *et al.,* 2010) [12]. This implies that acetylated starches which are significantly ($p < 0.05$) higher in oil absorption capacity than other starches will have a higher degree of flavor retention and mouth-feel than the other starches (Uzoma and Ibe, 2011) [40].

Table 5: Blue Value Index (%) of Cassava Starches as Affected by Modification Methods and Cassava Species

Chemical Modification Method						
Cassava Specie	**Native**	**Oxidation**	**Acetylation**	**Acid-thinning**	**Mean±SD**	**LSD**
NR 93/0199	1.67	2.17	2.17	2.67	2.17 ± 0.41^{b}	0.54
TMS 96/0304	2.50	2.67	2.83	3.17	2.79 ± 0.29^{a}	0.54
TMS 98/0581	0.83	1.83	2.33	2.67	1.92 ± 0.80^{b}	0.54
TMS 92/0326	1.33	2.33	2.17	2.33	2.04 ± 0.48^{b}	0.54
TMS 98/12123	1.33	1.83	2.33	2.33	1.96 ± 0.48^{b}	0.54
Mean±SD	1.53 ± 0.62^{c}	2.17 ± 0.36^{b}	2.37 ± 0.27^{ab}	2.63 ± 0.34^{a}		
LSD	0.46	0.45	0.46	0.46		

* Results are the means of triplicate samples ± SD
* Means with different superscripts differ significantly at $p < 0.05$
* LSD = least significant difference

Effects of Chemical Modification Methods and Cassava Species on Blue Value Index of Cassava Starches.

Table 5 shows the effects of chemical modification methods and cassava species on the blue value index of cassava starches. Acid-thinned starches had the highest blue value index (2.63%), though not significantly ($p < 0.05$) different from acetylated starches (2.37%) but differed significantly ($p< 0.05$) from other starches. The results showed that blue value index increased after modification processes of oxidization, acetylation and acid-thinning. This result is contrary to the report of Ibe (2010) which stated that the blue value index of cassava starches decreased after modification processes. Blue value index indicates the extent of the breakdown of the starch molecules in the native cassava starches (Abbey and Ibe, 1988). The results obtained showed that solubilization of amylose molecules seems to be more pronounced in acid-thinning method (Lawal, 2004) [21].

Cassava species affected the blue value index of cassava starches significantly ($p < 0.05$) with TMS 96/0304 recording the highest value of 2.79% and TMS 98/0581 recording the lowest value of 1.92%.

Table 6: Least Gelation Concentration (%) of Cassava Starches as affected by modification methods and cassava species

	Chemical Modification Method					
Cassava Specie	**Native**	**Oxidation**	**Acetylation**	**Acid-thinning**	**Total**	**Mean±SD**
NR 93/0199	8.00	10.00	12.00	6.00	36.00	9.00 ± 2.58
TMS 96/0304	6.00	8.00	10.00	6.00	30.00	7.50 ± 1.92
TMS 98/0581	10.00	6.00	12.00	8.00	36.00	9.00 ± 2.58
TMS 92/0326	8.00	6.00	12.00	6.00	32.00	8.00 ± 2.83
TMS 98/12123	8.00	6.00	10.00	8.00	32.00	8.00 ± 1.63
Mean±SD	8.00 ± 1.41^{b}	7.20 ± 1.79^{bc}	11.20 ± 1.10^{a}	6.80 ± 1.10^{bc}		
LSD	2.65	2.65	2.65	2.65		

* Results are the means of triplicate samples ± SD
* Means with different superscripts differ significantly at $p < 0.05$
* LSD = least significant difference

Table 7: Gelation Properties of Native, Oxidized, Acetylated and Acid-thinned Cassava Starches from NR 93/0199, TMS 96/0304, TMS 98/0581, TMS 92/0326, TMS 98/12123

	Chemical Modification Method			
Sample concentration (%)	**Native**	**Oxidation**	**Acetylation**	**Acid-thinning**
2.00	- Liquid	- Liquid	- Liquid	Liquid
4.00	- Liquid	- Liquid	- Liquid	Liquid
6.00	Viscous	Viscous	- Liquid	Viscous
8.00	Gel	Gel	- Liquid	Gel
10.00	Gel	Firm gel	Viscous	Firm gel
12.00	Firm gel	Firm gel	Gel	Firm gel
14.00	Firm gel	Firm gel	Firm gel	V. firm gel
16.00	V. Firm gel	v. firm gel	V. firm gel	V. firm gel
LGC	8.00	7.20	11.20	6.80

LGC = Least gelation concentration.

Gelation Properties

Taking the least gelation concentration as the index of gelation capacity, the gelation properties of native, oxidized, acetylated and acid-thinned cassava starches of NR 93/0199, TMS 96/0304, TMS 98/0581, TMS 92/0326 and TMS 98/12123 are presented in Tables 6 and 7. The lowest concentration for gelation (LGC) of native cassava starch was 8% ($^{w}/_{v}$). This value increased after acetylation, suggesting that native cassava starch is a better gelating food additive than acetylated cassava starch (Lawal, 2004) [21]. Acid-thinned cassava starches had the lowest value of 6.80% ($^{w}/_{v}$) as the least gelation concentration and was followed insignificantly ($p<0.05$) by oxidized cassava starches with a value of 7.20% ($^{w}/_{v}$). The result places acid-thinned cassava starch a much better gelating food additive than all the other starches (Lawal, 2004) [21].

The introduction of acetyl groups after modification caused inter-molecular repulsion in the starch gel, which accounts for weaker gels in acetylated cassava starches (Lawal, 2004) [21]. In contrast, in the present investigation, acid-thinning and oxidation improved gelation. The minimum concentration required for gelation in acid thinning was 6.80% ($^{w}/_{v}$), an improvement over 8.00% ($^{w}/_{v}$) of the native starch. This observation agrees with the earlier report of Wang and Wang (2001) on improvement of gelation capacity of corn starch, potato starch and rice starch following acid thinning. Acid-modified red bean starch and cassava starch was also reported to improve gel strength over the unmodified starch (Kim and Ahn, 1996; Be Miller and Whistler, 2009) [19, 3]. Ihekoronye and Ngoddy (1985) [11] reported that acid-thinned hydrolysis gives pastes which are prone to gel on cooling and form firmer gels than unmodified starch.

The crystalline region is an ordered arrangement of double helical amylopectin structures. Embedded in the amorphous region, amylose has been proposed to disrupt the crystalline packing of amylopectin (Moorthy, 2002; Lawal, 2004; Chanvrier *et al.*, 2007) [21]. In this sense, the erosion of the amorphous region by acid hydrolysis may result in a reduced hindrance of double helical chains approaching each other thus facilitating formation of Vander Waals forces and hydrogen bonding leading to stronger gelation properties (Nduele *et* al., 1993; Sandhu and Singh, 2007) [32]. There was no significant effect on the gelation properties of the cassava starches as a result of variation in species of the cassava.

Table 8: Effect of chemical modification and cassava specie on the viscosity (mPas) of the cassava starch.

	Chemical Modification Method				
Cassava Specie	Native	Oxidation	Acetylation	Acid-thinning	Mean±SD
NR 93/0199	98.20	98.20	98.25	98.10	98.19 ± 0.06[a]
TMS 96/0304	98.15	98.20	98.28	98.15	98.20 ± 0.06[a]
TMS 98/0581	98.35	98.30	98.15	98.15	98.24 ± 0.10[a]
TMS 92/0326	98.10	98.20	98.20	98.30	98.20 ± 0.08[a]
TMS 98/12123	98.10	98.30	113.00	98.15	101.28 ± 7.41[a]
Mean±SD	98.18 ± 0.01[a]	98.24 ± 0.06[a]	101.18 ± 6.61[a]	98.17 ± 0.08[a]	

***** Values are means of triplicates
* Means with different superscripts differ significantly at p<0.05.
* No significant (p> 0.05) difference existed due to variations both in cassava species and modification methods.

Effect of Chemical Modification and Cassava Specie on the Viscosity (mPas) of the Cassava Starch.

The results of the viscosities (mPas) of the cassava starches as affected by chemical modification methods and cassava species are presented in Table 8.

Acetylated starch had the highest viscosity (101.18 mPas) followed by oxidized starch (98.24 mPas) while acid-thinned starch had the lowest viscosity (98.17 mPas). The increase in viscosity of acetylated starch (though not significant at p<0.05) was as a result of disruption of the inter- and intra-molecular hydrogen bonds of the starch chains by the ester groups (Lawal, 2004) [21]. This weakened the granular structure of starch, leading to an increase in motional freedom of starch chains in amorphous regions (Thebaudin *et al.,* 1998). Ester groups are efficient in preventing amylose retrogradation (Lawal, 2004; Kawalijit *et al.,* 2007) [21]. Acetylation prevents gelling, weeping (syneresis) and maintains textural appearance. Wide applications are in foods as texturizing agents and provide good freeze-thaw stability (Kawalijit *et al.,* 2007). In paper industry, starch acetate can provide extremely good viscosity stability.

The decrease in the viscosity of the acid-thinned starch (Kim and Ahn, 1996) [19] was as a result of the attack by the hydroxonium ions on glycosidic oxygen atoms and hydrolysis of the glycosidic linkages (Wang and Wang, 2001; Lawal, 2004; Uzoma and Ibe, 2011) [21]. This cleaves chain length, decreases amylose content, increases solubility and lowers viscosity (Kim and Ahn, 1996; Lawal, 2004) [19, 21]. Acid-thinning increases tendency to retrogradation (Kawalijit *et al.,* 2007). The lower viscosity permits higher concentration to be used for forming rigid gels in gums, pasteries and jellies. According to Lawal (2004) [21] oxidation involves introduction of carboxyl and carbonyl functional groups with subsequent de-polymerization of the starch. Oxidation reduces the tendency to retrogradation producing soft-bodied gels of high clarity. Oxidized starches are the best thickeners for applications requiring gels of low rigidity. This improves adhesion in butter and bread. Diluted solution of highly oxidized starches, remain clear on prolonged storage, making them suitable for clear, canned soups and transparent confectionery products (Kawalijit *et al.,* 2007). Oxidized starch is also widely used in surface sizing for paper industry, wrap sizing in textile industry, in lemon curd manufacture, in salad creams and mayonnaises (Lawal, 2004; Kawalijit *et al.,* 2007) [21].

For the cassava species, the viscosity values (though not significant at p<0.05) range from 101.88 mPas in TMS 9812123 to 98.19 mPas in NR 93/0199. This result projects cassava specie, TMS 98/12123 as a good source of starch for making texturizing agents.

Conclusion

The three chemical modification methods (oxidation, acetylatation and acid-thinning) affected significantly (p<0.05) the functional properties and baking potentials of the five selected improved cassava species. These improved cassava species (NR 93/0199, TMS 96/0304, TMS 98/0581, TMS 92/0326 and TMS 98/12123) exhibited different functional properties significantly (p<0.05).

Acetylated starches had highest values in oil absorption capacity (85.60%), least gelation concentration (11.20%) and swelling power (31.07%) whereas acid-thinned starches led in blue value index (2.63%) and solubility (34.50%). TMS 98/12123 had highest values in solubility (30.86%) and oil absorption capacity (77.59%). These information provided will promote the efficient utilization and application of cassava starches in a variety of industries for the manufacture of confectioneries, thickeners, stabilizers, binders, fillers, flavouring agents, cheese, soups, sauces, gravies, coating system, dairy products, beverage and bakery products.

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