Journal of Plant Breeding and Crop Science Vol. 3(9), pp. 195-202, 15 September, 2011
Available online http://www.academicjournals.org/jpbcs
ISSN 2006-9758 ©2011 Academic Journals

Full Length Research Paper

Amylopectin molecular structure and functional properties of starch from three Ugandan cassava varieties

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Accepted 13 July, 2011

Amylopectin molecular structure is a very important determinant of starch functional properties. The main purpose of this study was to determine the strength of the relationship between the amylopectin structure of starches from cassava varieties and their functional properties. TME14 had the highest (46.63%) proportion of A chains while Bamunanika had the lowest 42.27%. Bamunanika had the highest (23.33%) proportion of $B3^{+}$ chains while TME14 had the lowest 19.66%. TME14 had the highest amylopectin molecular weight $2.74x10^{8}$ g/mol while NASE10 had the lowest $2.42x10^{8}$ g/mol. TME14 had a higher gelatinisation temperature 65.37°C compared to the other varieties. Bamunanika had the highest final viscosity 2477.66 mPa s while NASE10 had the highest set back viscosity (494.50 mPa s). TME14 had the highest pasting temperature 67.80°C while NASE10 had the lowest 65.23°C. There was a significant negative correlation between final viscosity and A chains (r = -0.64), pasting temperature and A chains (r = - 0.77), A, B1 chains and gelatinisation temperature of retrograded starches (r = - 0.82, r = - 0.87), respectively, gyration radius and onset temperature of gelatinisation for the retrograded starch (r = -0.56) and a significant positive correlation between B2 chains and pasting temperature (r = 0.94), amylopectin molecular weight and percentage retrogradation (r = 0.66). These findings revealed possible improvement through breeding for starch with desired qualities.

Key words: Amylopectin structure, cassava varieties, functional properties.

INTRODUCTION

Cassava (*Manihot esculenta* Crantz) is one of the most important sources of commercial starch in tropical and subtropical countries (Moorthy, 2004); it is widely used in tropical Africa and in parts of Asia, particularly Indonesia and Thailand (Ernesto et al., 2000). Uganda relies on imported starches resulting in increased costs of production. Late deliveries for imported starches has been a major challenge affecting industrial productivity in Uganda compelling producers to search for cheaper locally processed starch alternatives (Graffham et al., 2000). The study, therefore profiled starches from cassava varieties available in Uganda to enable their full exploitation to benefit both cassava farmers and starch industries. Cassava varieties bred by the National Crops Resources Research Institute (NaCRRI) showed considerable differences in their functional properties (Nuwamanya et al., 2009). Bello-Perez et al. (1998) reported that amylopectin molecular structure could be used to indicate the possible uses of starches and predict their behaviour when incorporated into the food system or other industrial applications. Ramesh et al., (1999) and Patindol and Wang (2002) suggested that there was a correlation between amylopectin molecular structure and functional properties of starchy materials. Ong and Blanshard (1995) reported that rice with a higher amylose content and more long chain amylopectin tended to be hard after cooking while Mua and Jackson (1997) reported that molecular weight and extent of molecular

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branching affected retrogradation. Starches isolated from 3 cassava varieties were analysed to determine the variation in molecular structure among these varieties and relationship of molecular structure and the functional properties.

MATERIALS AND METHODS

Maize, LEB8004 and Kenya tapioca were commercial starches for comparison with starch from Ugandan cassava varieties NASE10, TME14 and Bamunanika. Field experiments were set up at the national crops resources research institute (NaCRRI), Namulonge, in central Uganda. The three varieties were selected because they are representative of the cassava varieties grown in Uganda. TME14 is a farmer preferred landrace from Nigeria; NASE10 is an elite improved cassava variety and Bamunanika is a farmer preferred Ugandan land race.

Harvesting and collection of root samples

The cassava roots were harvested at 12 months after planting. The roots were prepared for starch extraction by peeling and washing with distilled water.

Starch extraction

Native cassava starch extraction was carried out using a method described by Benesi (2005) and Nuwamanya et al. (2009). The starch was air dried on aluminium pans at room temperature for 24 to 36 h and stored in plastic air tight containers at room temperature.

Moisture content of native starch

Moisture content (MC) was determined using 1.5 g starch according to International Starch Institute (ISI) method, (1997) using the formula;

$MC\% = 100 \times (W1-W2) / W1$

Where W_1= Weight of starch sample before oven drying

W_2= Weight of starch sample after oven drying

Determination of bound lipids

The bound lipids of the starch samples were determined using a standard method by Helrich (1990) by extraction using a hexane chloroform mixture (1:1 v/v). The residue was dried in an oven for 2 h at 105°C and it was weighed. The difference in weight of the original and extracted sample was used to calculate the percentage lipid content.

Determination of the ash content

The ash content was determined using a standard method by Helrich, (1990). 1.0 g starch was heated in a furnace at 550°C for 8 h. The residue was weighed and the ash content was calculated as the percentage difference.

Determination of amylose content

Amylose content was determined from 0.5 g starch (dry weight basis) using the Megazyme amylose/amylopectin assay kit (Megazyme International Ireland, Bray Business Park, Bray, Ireland) by selective quantitative precipitation of amylopectin with concanavalin A (Con A), quantitative estimation of amylose on hydrolysis using amylase/amyloglucosidases and estimation of glucose by glucose oxidase/peroxidase assay.

Gelatinization properties

The gelatinisation properties of starch were analysed using a differential scanning calorimeter (DSC Q2000 V24.4 Build 116) equipped with a thermal analysis data station. Starch (3 mg, dry starch basis) was weighed in an aluminium pan then 6 µL of double distilled water was added. Therefore the starch to water ratio was 1:2. The samples were hermetically sealed and allowed to equilibrate overnight at room temperature. An empty sealed pan was used as a reference. The scanning temperature range was 20 to 140°C and the heating rate was 10°C/min. Onset temperature (To), peak temperature (Tp) and enthalpy change were given directly by the DSC software.

Retrogradation properties

After storage at 4°C for 7 days, the previously gelatinised starch samples were removed from the refrigerator and allowed to equilibrate at room temperature for 1 h, then rescanned by DSC using the same heating parameters as for the gelatinisation process (The scanning temperature range was 20 to 140°C and the heating rate was 10°C/min). Onset temperature (To), peak temperature (Tp) and enthalpy change were given directly by the DSC software. The reference was prepared the same way as described in the gelatinisation section.

Pasting properties

The viscosity and pasting properties of the starch samples were determined using a rapid visco analyser (RVA) (Series 4V, Newport Scientific Pty. Ltd, Warriewood, Australia) using standard profile 1. The samples were mixed with double distilled water in the canister at a concentration of 7% (2 g db in 18 g total), for at least 30 s. After placing the canister in the RVA, the sample was stirred for 60 s at 50°C, heated to 95°C at a rate of 13°C/3.8 min and finally held at 50°C for 2 min, all at a rotation speed of 160 rpm. Total running time was 13 min. Duplicate analyses were performed on each sample and the results were averaged.

Determination of Amylopectin branch chain distribution

Amylopectin branch chain distribution was determined using the high performance liquid chromatography (HPLC) method. Starch was solubilised according to Jane et al. (1992). Amylopectin was debranched according to Lin et al. (2006). The mixture was passed through a 0.45 µm nylon filter and then injected via a 50 µL (ca. 0.18 mg/mL) loop injector (Rheodyne 7125). Solvent (0.007M ammonium sulphate/acetic acid buffer), pH 3, passed through a 0.45 µm Millipore filter was delivered to the column at a flow rate of 0.4 mL/min with a Varian 9012HPLC pump and the chromatogram was recorded from the response of a refractive index detector (Varian Star 9040, Gen Tech Scientific, Inc. Arcade, NY, USA). Data were collected and analysed by Varian Galaxie chromatography workstation software version 4.51. The number-average molar mass (M_n) was estimated from calibration curve made with various molar mass pullulan standards (5900, 11800, 22800, 47300, 112000 and 212000 g/mol) (polymer Laboratories, Amherst, USA).

Table 1. Proximate composition of starches from Ugandan cassava varieties.

Sample	% LC	%AM	% MC	% AC
Bamunanika*	0.22^{c}±0.01	22.85^{c}±0.02	15.87^{a}±0.01	0.19^{c}±0.01
NASE 10*	0.28^{b}±0.01	18.95^{f} ±0.01	15.75^{a}±0.01	0.24^{a}±0.00
TME 14*	0.19^{d}±0.01	24.67^{b}±0.01	15.59^{a}±0.01	0.22^{b}±0.01
Kenya Tapioca	0.09^{e}±0.00	20.35^{e}±0.01	12.28^{b}±0.16	0.19^{c}±0.01
LEB 8004	0.09^{e}±0.00	21.44^{d}±0.02	11.76^{c}±0.25	0.19^{d}±0.01
Maize	0.50^{a}±0.00	28.55^{a}±0.01	11.67^{d}±0.14	0.20^{c}±0.00
%CV	3.07	0.07	1.11	3.41
LSD (P< 0.05)	0.017	0.030	0.371	0.015

Uganda cassava varieties*, Values were calculated from two replicates; ± standard deviation. Results followed by the same superscript in a column were not significantly different at P<0.05. LC = Lipid content; AM = amylose content; MC = moisture content; AC= ash content.

A regression coefficient (R^2) between log molar mass and retention time of 0.991 was obtained. The chain lengths (DP_n) of the branches were calculated by dividing M_n by 162.

Determination of amylopectin molecular weight, radius of gyration and polydispersity

Amylopectin molecular weight, radius of gyration and polydispersity were determined using the high performance size exclusion chromatography (HPSEC-MALLS-RI) method. Starch was solubilised according to Jane et al. (1992). The starch precipitate was dried in a vacuum dessicator. 4 mL of double distilled water was put into precipitate with a stir bar and heated in a boiling hot water bath for 20 min with continuous stirring. The mixture was passed through a 5 µm nylon filter then injected into the column through a 200 µL loop injector (Rheodyne 7125, Cotati, CA, USA). Fractionation of the starch components was made on a SEC column (Sephacryl S-500 HR, dextran exclusion range Mr = $4.0x10^4$-$2.0x10^7$ g/mol, GE HEALTH SCIENCE). The solvent (water with 0.02% sodium azide) used for elution was passed through a 0.1 µm Millipore filter, degassed and pumped (Shimadzu, LC-10ATVP, Kyoto, Japan) isocratically to the column at a flow rate of 1.3 mL/min. The data collected from the response of an on-line MALLS Laser photometer (DAWN DSP-F, wavelength 488.0 nm with a K-5 flow cell) and DRI (Wyatt/Optilab 903) was analysed for Mw, Mn, Pd, Rz by Astra for Windows software (version 5.3.4.14, 2008) (Wyatt Technology Corp., Santa Barbara, CA, USA).

Statistical analysis

Quantitative data was subjected to analysis of variance (ANOVA) using the general linear model (GLM) procedures of SAS (SAS, 2003), (SAS Institute Inc., Cary, NC, USA). Means were calculated for each of the starch parameter and the least significant difference (LSD) was used to separate the means at P<0.05. Pearson correlation coefficients were computed to establish the relationship between the amylopectin molecular structure and starch functional properties.

RESULTS AND DISCUSSION

Proximate composition of starch samples

The results for the proximate chemical composition of the starch samples are presented in Table 1. The results showed that starch moisture content for the cassava varieties ranged from 15.59 to 15.87%, which was within the 10 to 20% range recommended for commercial starches (Soni et al., 1993). The ash content of cassava starches ranged from 0.19 to 0.24%, well below the limit of 0.5% recommended for grade A industrial starches (Radley, 1976) and lipid content ranged from 0.19 to 0.28% which compared favourably with the previously reported range of 0.11 to 0.2% for cassava starch (Moorthy, 2002; Daramola and Osanynlusi, 2006). The results clearly indicated that the cassava varieties had starches of high purity and met the worldwide industrial standards.

Functional properties

Gelatinisation properties

The results of gelatinisation properties determined by differential scanning calorimetry (DSC) are presented in Table 2. The low gelatinisation transition temperatures exhibited by the starches from the three cassava varieties could be attributed to their higher proportions of amylopectin short branch chains as postulated by Noda et al. (1998). Bamunanika and NASE10 with lower gelatinisation temperatures would be more suitable for the textile industry and in the production of products with thermolabile ingredients such as vitamins and proteins in pharmaceuticals, baby food and pie fillings which require less heat treatment. TME14 with a high gelatinisation temperature would be suitable in applications that require high processing temperature such as canned foods and bread products (Betancur-Ancona et al., 2001).

Retrogradation

The results of retrogradation properties of the starches are presented in Table 3. Cassava starches had lower

Table 2. Gelatinisation properties of starches from Ugandan cassava varieties.

Sample	T_OG (°C)	T_PG (°C)	ΔH (J/g)
Bamunanika*	58.39^{e}±0.12	63.76^{e}±0.53	11.65^{b}±0.07
NASE 10*	58.98^{e}±0.29	63.60^{e}±0.20	11.24^{b}±0.74
TME14*	59.85^{d}±0.42	65.37^{d}±0.48	10.19^{c}±0.24
Kenya Tapioca	63.72^{b}±0.19	68.54^{b}±0.21	11.80^{b}±0.48
LEB 8004	62.08^{c}±0.30	67.37^{c}±0.28	12.57^{b}±0.00
Maize	64.70^{a}±0.27	69.90^{a}±0.21	13.17^{a}±0.07
%CV	0.46	0.51	3.24
LSD (P<0.05)	0.69	0.82	0.92

Uganda cassava varieties*, ToG = onset temperature of gelatinisation; TpG = peak temperature of gelatinisation; ΔH = gelatinisation enthalpy in J/g. Results followed by the same superscript in a column were not significant ly different at P<0.05.

Table 3. Retrogradation properties of starches from Ugandan cassava varieties.

Sample	T_O (°C)	T_P (°C)	ΔH (J/g)	% R
Bamunanika*	46.04^{a} ±0.35	53.05^{a}±0.41	2.10^{b}±0.10	18.05^{b}±0.78
NASE 10*	46.91^{a}±1.27	53.35^{a}±0.71	1.60^{c}±0.01	14.26^{b}±1.08
TME14*	45.42^{a}±0.07	53.05^{a}±0.40	1.73^{bc}±0.30	17.06^{b}±3.38
LEB 8004	42.25^{bc}±0.78	51.11^{b}±0.37	1.94^{bc}±0.07	16.00^{b}±0.64
Kenya tapioca	44.41^{ab}±0.29	52.38^{a}±0.33	1.81^{bc}±0.26	15.34^{b}±1.59
Maize	41.70^{c}±1.96	51.01^{b}±0.04	5.25^{a}±0.12	39.85^{a}±1.20
%CV	2.03	0.81	7.47	8.53
LSD(P<0.05)	0.69	0.82	0.92	4.16

Uganda cassava varieties*, To = onset temperature; Tp = peak temperature; ΔH = enthalpy change of starch retrogradation at 4°C for 7 days; Percentage retogradation (%R) = ΔH (gelatinisation of retrograded starch) / ΔH gelatinisation of native starch) x 100. Results followed by the same superscript in a column were not significant ly different at P<0.05.

retrogradation rates compared to maize starch. Similar results were reported by Jane et al. (1999) where cereal starches retrograded more rapidly than the root starches. The lower retrogradation percentage for cassava starch could be attributed to the larger proportion of amylopectin short branch chains as reported by Lu et al. (1997), Shi and Seib (1992) and presence of phosphate monoesters in root starches (Jane et al., 1999; Lim et al., 1994) which retard retrogradation rates. The results suggested that cassava starch was more stable than maize starch under storage which makes cassava starches suitable in making products stored for a long time and in which soft texture is necessary such as dessert-like products.

Starch viscosity and pasting properties

The results of starch pasting properties are presented in Table 4. Starch pasting properties were significantly (P<0.05) different among the different cassava varieties, this could be attributed to the genetic variation which has been reported to induce differences in pasting and viscoelastic characteristics of starch by Asaoka et al. (1992).

NASE10 with the highest breakdown viscosity of 1208.30 mPa s was considered inferior to the other cassava varieties, because its viscosity rapidly lowered on heating under shear leading to a long and cohesive texture of its paste, which is not desired in textile applications.

The high set back viscosity of NASE10 494.50 mPa s compared to the other cassava varieties would limit its application in the food and textile industries (Moorthy, 2002). The differences observed in setback viscosity among the cassava varieties reflected the different thermodynamic behaviours of these starches during heating which play important roles in industrial applications.

The high final viscosity exhibited by Bamunanika (2477.66 mPa s) makes it more suitable in many food products such as sauces, soups, dressings and in the textile and the wet stage of paper making where high viscosity is desired (Moorthy, 2002), while the low final viscosity of NASE10 1808.00 mPa s makes it more suitable in the dry stage of paper production where lower viscosity and good film forming capacity are preferred (Moorthy, 2002).

The low pasting temperature of NASE10 and Bamunanika starches suggested that they easily formed pastes hence more suitable in most food and non food

Table 4. Viscosity and pasting properties of starches from Ugandan cassava varieties.

Sample	BD (mPa s)	FV (mPa s)	SB (mPa s)	PT (^{o}C)
Bamunanika*	790.66^{d}±7.50	2477.66^{a}±11.00	412.62^{d}±0.70	65.45^{d}±0.74
TME14*	709.34^{e}±8.30	2010.33^{b}±10.00	446.49^{c}±2.12	67.80^{c}±0.08
NASE10*	1208.30^{c}±9.70	1808.00^{c}±10.60	494.50^{a}±0.70	65.23^{d}±0.11
LEB8004	1380.38^{b}±8.50	1577.66^{d}±11.00	474.56^{b}±2.12	68.58^{c}±0.07
Kenya tapioca	1574.29^{a}±9.60	1532.54^{e}±7.50	492.00^{a}±2.82	70.22^{b}±0.10
Maize	427.00^{f}±7.00	1576.63^{d}±11.20	354.00^{e}±2.82	76.70^{a}±0.80
CV%	0.78	0.43	0.46	0.41
LSD (p<0.05)	19.39	19.62	5.09	0.68

Uganda cassava varieties*, Values were calculated from two replicates; ± standard deviation.Results followed by the same superscript in a column were not significantly different at P<0.05. mPa s = MilliPascal seconds, A unit for measuring dynamic viscosity. BD = break down viscosity; FV = Final viscosity; SB= Set back viscosity, PT = Pasting temperature.

Table 5. Percentage branch chain length distribution of amylopectin from starches of Ugandan cassava varieties.

Sample	% branch chain distribution			
	A chain	B1 chain	B2 chain	B3^{+} chain
Bamunanika*	42.27^{d}±0.04	24.56^{a}±0.15	9.84^{a}±0.09	23.33^{a}±0.01
NASE 10*	45.67^{b}±0.04	23.00^{c}±0.45	9.30^{ab}±0.07	21.98^{ab}±0.59
TME14*	46.63^{ab}±0.38	24.53^{a}±0.12	9.14^{b}±0.03	19.66^{bc}±0.23
LEB 8004	44.97^{bc}±1.61	25.02^{a}±0.74	9.66^{ab}±0.67	22.19^{ab}±2.87
Kenya tapioca	43.68^{cd}±1.08	23.51^{bc}±0.04	9.2^{ab}±0.02	23.55^{a}±1.14
Maize	48.04^{a}±0.01	24.08^{ab}±0.41	8.95^{b}±0.03	18.84^{c}±0.39
%CV	1.78	1.66	3.01	6.01
LSD(P<0.05)	1.97	0.98	0.69	3.17

Uganda cassava varieties*, Values were calculated from two replicates; ± standard deviation. Results followed by the same superscript in a column were not significantly different at P<0.05. Each chain was classified into one of the four fractions according to its degree of polymerisation (DP), A= (DP < 12); B1 = (DP 13-24); B2 = (DP 25-36); B3^{+}= (DP > 37) (According to Hanashiro et al., 1996).

industrial processes because of reduced energy costs during production processes. The wide variation in the pasting temperature among the cassava varieties offered more opportunities for utilisation of cassava starches in several industries.

Amylopectin branch chain distribution

The results of amylopectin branch chain distribution are presented in Table 5. Amylopectin branch chains were classified into chain types and corresponding degree of polymerization (DP) according to Hanashiro et al. (1996) as follows; A chain (DP <12), B1 chain (DP 13-24), B2 (DP 25-36) and B3^{+} chain (DP > 37). There were significant (P<0.05) differences in the amylopectin branch chain distributions among the starches from the cassava varieties. Maize starch had more A chains while cassava starches had more B2 and B3^{+} chains (Table 5). Similar results were previously reported by Hizukuri (1985, 1986) who reported that cereal starches had higher proportions of A chains compared to root starches. Among the Ugandan cassava varieties TME14 had the highest proportion of A chains (46.63%) while Bamunanika had the lowest 42.27%. The high proportion of short A chains has been associated with low starch retrogradation rates (Shi and Seib, 1992; Kalichevsky et al., 1990; Wursch and Gumy, 1994) and low starch gelatinisation temperature (Jane et al., 1999; Silverio et al., 2000). Bamunanika had the highest 23.33% proportion of B3^{+} chains while TME14 had the lowest 19.66%. The high proportion of B3^{+} chains has been associated with high gelatinisation temperature (Srichuwong et al., 2005) and high pasting temperature (Jane et al., 1999).

Amylopectin molecular weight (Mw), Radius of gyration (Rz) and polydispersity (pds)

The results for molecular weight, polydispersity and gyration radius are presented in Table 6. There were significant (P<0.05) differences in molecular weight and gyration radius among the starches from the three cassava varieties. Molecular weights of the amylopectin molecules for the cassava varieties ranged from 2.42

Table 6. Amylopectin molecular weight, gyration radii and polydispersity of starches from Ugandan cassava varieties.

Sample	Mw x10^8(g/mol)	Rz (nm)	Polydispersity
Bamunanika*	2.56^b±0.09	170.50^b±5.65	1.18^a±0.04
NASE 10*	2.42^b±0.14	176.50^b±4.66	1.10^a±0.01
TME14*	2.74^b±0.21	172.55^b±4.03	1.15^a±0.00
LEB 8004	3.19^a±0.25	193.10^a±0.56	1.10^a±0.02
Kenya tapioca	2.72^b±0.09	171.2^b±3.67	1.14^a±0.01
Maize	3.33^a±0.03	178.10^b±1.13	1.19^a±0.09
%CV	5.60	2.12	4.01
LSD(P<0.05)	0.38	9.21	0.11

Uganda cassava varieties*, Values were calculated from two replicates; ± standard deviation.Results followed by the same superscript in a column were not significantly different at P<0.05. Mw = Molecular weight; Rz = average radius of gyration.

x10^8 (NASE 10) to 2.74x10^8 g/mol (TME14) suggesting that TME14 starch had more densely packed molecules compared to the other cassava varieties. Yoo and Jane (2002) reported that amylopectin molecules with higher molecular weight had more branch chains and more densely packed molecules. Molecular weight has been associated with starch solubility with Mizukami et al. (1999) reporting that small amylopectin molecules dissolve more easily in hot water than the large molecules implying that NASE10 with lower amylopectin molecular weight would have high solubility compared to TME14, therefore making NASE10 more important in applications such as pharmaceuticals (Moorthy, 2002) for easy release of the active ingredients in the pharmaceuticals and in the food industry such as baby food, yoghurt and dessert like products, where high solubility was associated with good cooking and eating qualities (Moorthy, 2002).

Starch solubility also allows easy hydrolysis to release glucose for use by the organism. Amylopectin molecular weight has also been reported to influence the pasting viscosity of starch (Bultosa et al., 2008). Larger molecular weight amylopectin molecules have capability of inter and intra-molecular interactions thus making them more difficult to dissolve in hot water which may affect starch pasting properties. Rice volume expansion, paste peak and final viscosity have been associated with high amylopectin molecular weight and radius of gyration (Patindol et al., 2006). An increase in amylopectin molecular weight has been reported to decrease the amount of long-branch chain length as well as branching degree of amylopectin resulting into an increased peak and breakdown viscosity, decrease in setback and final viscosity (Takeda et al., 1989) thus making such starch unsuitable in textile and paper industries where high final viscosities are desired.

Correlations between amylopectin molecular structure and starch functional properties

Several significant correlations between amylopectin molecular structure and functional properties were observed (Table 7). There was a significant negative correlation between final viscosity and A chains (DP<12) (r = -0.64). This was attributed to the weak interactions of the short branch chains which do not hold the integrity of the swollen granules resulting into granule disruption during heating leading to a reduced final viscosity (Stevenson, 2003). A higher proportion of long chains have been reported to contribute to high viscosity because long chains increase the gyration radius of amylopectin molecules (Whistler and BeMiller, 1997). There was a significant negative correlation between pasting temperature and A chains (DP<12) (r = - 0.77), suggesting that short chains do not contribute to a high crystalline quality and hence less energy would be required to melt the starch crystallinity resulting in a low pasting temperature (Jane et al., 1999). There were significant negative correlations between A, B1 chains and gelatinisation temperature of retrograded starches (r = -0.82, r = -0.87), respectively. This was attributed to the high proportion of short branch chains (A and B1) which do not easily reassociate on cooling and therefore inhibit retrogradation (Kalichevsky et al., 1990; Shi and Seib, 1992; Wursch and Gumy, 1994; Lu et al., 1997).

The significant negative correlation between gyration radius and onset temperature of gelatinisation for the retrograded starch (r = -0.56) was attributed to the more free movement of longer linear chains in the amylopectin polymer (Klucinec and Thompson, 1999) hence, readily forming double helices during cooling leading to high rates of retrogradation. There was a significant positive correlation between amylopectin molecular weight and percentage retrogradation (r = 0.66) attributed to the decreased degree of branching resulting from increased amylopectin molecular weight (Takeda et al., 1989). The significant positive correlation between B2 chains (DP25-36) and pasting temperature (r = 0.94) indicated a high crystallinity quality as a result of long branch chains (Jane et al., 1999) which required more energy to melt hence high pasting temperature and this implied that starch with a high proportion of long chains is associated with high energy costs. These findings showed that amylopectin

Table 7. Pearson correlation matrix for starch functional properties and amylopectin molecular structure.

	BD	FV	SB	PT	ToG	TpG	ΔHG	ToR	TpR	ΔHR	%R
A	0.22	-0.64*	-0.25	-0.77*	0.71**	0.69	0.72	-0.40	-0.82*	-0.52	0.56
B1	0.42	0.07	0.15	-0.62	-0.11	-0.22	0.72	0.36	-0.87*	-0.63	-0.09
B2	-0.05	-0.67*	0.16	0.94**	-0.73**	0.75***	-0.86	0.74**	0.86	0.42	-0.41
B3	-0.80	0.47	0.32	0.19	-0.67*	-0.66	-0.18	0.39	0.16	-0.14	-0.54
Mw	-0.27	-0.52	-0.50*	-0.07	0.71**	0.76***	0.73	-0.88***	-0.19	-0.67	0.66*
Rz	0.11	-0.47	0.11	0.22	0.22	0.24	0.08	-0.56*	0.08	-0.09	0.05
Pds	0.10	0.26	-0.62*	-0.29	0.18	0.23	-0.08	0.01	0.14	0.039	0.50*

*, **, and *** = significant at p<0.1, 0.01, and 0.005, respectively. Functional properties; BD = break down viscosity; FV = Final viscosity; SB = Set back; PT = pasting temperature; ToG = onset gelatinization temperature, TpG = gelatinization temperature; ΔHG = enthalpy of gelatinization; ToR, Onset temperature after retrogradation; TpR, gelatinisation temperature after retrogradation; ΔHR enthalpy after retrogradation; %R = Percentage retrogradation. Amylopectin molecular structure; Mw = molecular weight; Rz = radius of gyration, Pds = polydispersity; A chain= (DP < 12); B1 = chain (DP 13-24); B2 = (DP25-36); $B3^{+}$= (DP > 37).

molecular structure was a critical factor influencing starch functional properties.

Conclusion

Cassava starches of different varieties differed in their functional properties and the molecular structures. Correlation analysis provided valuable information on the influence of amylopectin molecular structure on starch functional properties. The correlation analysis suggested the possibility of using amylopectin molecular structure in the selection of cassava lines with desired starch functional properties for different industries.

ACKNOWLEDGEMENTS

This work was supported under the BIO-EARN program, with a grant from the Swedish International Cooperation Agency/Department for Research Cooperation (Sida/SAREC). We also thank Dr. Hamaker Bruce of the Whistler Center for Carbohydrate Research, Department of Food Science, Purdue University.

REFERENCES

Asaoka M, Blanshard JMV, Rickard JE (1992). Effect of cultivar and growth season on the gelatinization properties of cassava (Manihot esculenta) starch. J. Sci. Food Agric., 59: 53-58.

Bello-Perez LA, Roger P, Baud B, Colonna P (1998). Macro-molecular features of starches determined by aqueous high-performance size exclusion chromatography. J. Cereal Sci., 27: 267-278.

Betancur-Ancona DA, Chel-Guerrero LA, Camelo-Matos RI, Ortiz-Davila G (2001). Physicochemical and functional characterization of baby lima vean (Phaseolus lunatus) starch. Starch/Starke, 53: 219-226.

Bultosa G, Hamaker BR, Bemiller JN (2008). An SEC-MALLS study molecular features of water soluble amylopectin and amylose of Tef (*Eragrostis tef (Zucc.)* Trotter] starches. Starch/Stärke, 60: 8-22.

Daramola B, Osanynlusi F (2006). Enhancement of agronomical values, upstream and downstream opportunities for starch and starch adjuncts. Afr. J. Biotechnol., 5(25): 2488-2494.

Ernesto M, Cardoso AP, Cliff J, Bradbury JH (2000). Cyanogens in cassava flour and roots and Urinary thiocynate concentration in Mozambique. J. Food Compos. Anal., 13: 1-12

Graffham A, Kleih U, Jagwe J, Nabawanuka J, Wanda K, Kalunda P, Ntibarikure G (2000). Industrial markets for starch based products. An assessment of the industrial potential in Uganda, IITA and NARO, graffham@gre.ac.uk.

Helrich K (1990). Official Methods of Analysis 15th Edition. Association of Official Analytical Chemist Inc., Virginia, p. 70.

Hizukuri S (1985). Relationship between the distribution of the chain length of amylopectin and the crystalline structure of starch granules. Carbohydr. Res., 141: 295-306.

Hizukuri S (1986). Polymodal distribution of the chain lengths of amylopectins, and its significance. Carbohydr. Res., 147: 342-347.

ISI (1997). Tapioca (Cassava) starch. Available at URL:http:// home3.inet.tele.dk/starch/isi/.

Jane J, Chen J, McPherson AE, Wong KS, Radosavljevic M, Ksemsuwan T (1999). Effects of amylopectin branch chain length and amylose content on the gelatinisation and pasting properties of starch. Cereal Chem., 76: 629-637.

Jane J, Xu A, Radosavlijevic M, Seib PA (1992). Location of amylose in normal starch granules. I. Susceptibility of amylose and amylopectin to cross-linking reagents. Cereal Chem., 69: 405-409.

Kalichevsky MT, Orford PD, Ring SG (1990). The retrogradation and gelation of amylopectin from various botanical sources. Carbohydr. Res., 198: 49-55.

Klucinec J, Thompson D (1999). Amylose and amylopectin interaction in retrogradation of dispersed high-amylose starches. Cereal Chem., 76: 282-291.

Lim ST, Kasemuswan T, Jane J (1994). Characterisation of phosphorus in starches using 31P-NMR spectroscopy. Cereal Chem., 7: 488-493.

Lin H M, Chang Y, Lin J, Jane J, Sheu M, Lu T (2006). Heterogeneity of lotus rhizome starch granules as revealed by alpha-amylase degradation. Carbohydr. Polym., 66: 528-536.

Lu S, Chen LN, Lii CY (1997). Correlations between the fine structure, physicochemical properties, and retrogradation of amylopectins from Taiwan rice varieties. Cereal Chem., 74: 34-39.

Mizukami H, Takeda Y, Hizikuri S (1999). The structure of the hot water soluble components in the starch granules of new Japanese rice cultivars. Carbohydr. Polym., 38: 329-335.

Moorthy SN (2002). Physicochemical and functional properties of tropical tuber starches. Starch/Starke, 54: 559-592.

Moorthy SN (2004). Tropical sources of starch. In: Eliasson A.C. Starch in food: Structure, function and applications (pp. 321-359). Cambridge and New York: Woodhead Publishing Limited and CRC Press LLC.

Mua J, Jackson D (1997). Relationships between functional attributes and molecular structures of amylose and amylopectin fractions from corn starch. J. Agric. Food Chem., 45: 3848-3854.

Noda T, Takahata Y, Sato T, Suda I, Morishita T, Ishiguro K,

Yamakawa O (1998). Relationships between chain length distribution of amylopectin and gelation properties within the same botanical origin for sweet potato and buckwheat. Carbohydr. Polym., 37: 153-158.
Nuwamanya E, Baguma Y, Kawuki RS, Rubaihayo PR (2009). Quantification of starch physicochemical characteristics in a cassava segregating population. Afr. Crop Sci. J., 16(3): 191-202.
Ong M, Blanshard J (1995). Texture determinants of cooked, parboiled rice. II. Physicochemical properties and leaching behaviour of rice. J. Cereal Sci., 21: 261-269.
Patindol J, Flowers M, Wang Y, Gealy D (2006). Comparison of physicochemical properties of starches from red rice and cultivated rice. J. Agric. Food chem., 54: 2712-2718.
Patindol J, Wang YJ (2002). Fine structure of starches from long grain rice cultivars with different functionality. Cereal Chem., 79:465-469.
Ramesh M, Alin S Z, Bhattacharya K R (1999). Structure of rice starch and its relation to cooked rice texture. Carbohydr. Polym., 38(4): 337-347.
Shi Y-C, Seib PA (1992). The structure of four waxy starches related to gelatinisation and retrogradation. Carbohydr. Res., 227: 131-145.
Silverio J, Fredriksson H, Andersson R, Eliasson AC, Aman P (2000). The effect of temperature cycling on the amylopectin retrogradation of starches with different amylopectin unit-chain length distribution. Carbohydr. Polym., 42: 175-184.
Soni PL, Sharma H, Dun D, Gharia MM (1993). Physicochemical properties of Quercus leucotrichophora (Oak) starch. Starch/Starke, 45(4): 127-130.
Srichuwong S, Sunarti TC, Mishima T, Isono N, Hisamatsu M (2005). Starches from different botanical sources I: Contribution of amylopectin fine structure to thermal properties and enzyme digestibility. Carbohydr. Polym., 60: 529-538.
Stevenson DG (2003). Role of starch structure in texture of winter squash (*Cucurbita maxima* D.) fruit and starch functional properties. PhD. Dissertation. Iowa State University. Ames. Iowa. U.S.A.
Takeda Y, Murata N, Hizukuri S, Juliano BO (1989). Structures of indica rice starches (IR48 and IR64) having intermediate affinities for iodine. Carbohydr. Res., 187: 287-294.
Whistler L, BeMiller JN (1997). Carbohydrates chemistry for food scientists. AACC, Inc., St. Paul, MN, USA.
Wursch P, Gumy D (1994). Inhibition of amylopectin retrogradation by partial beta-amylosis. Carbohydr. Res., 256: 129-137.
Yoo S, Jane J (2002). Structural and physical characteristics of waxy and other wheat starches. Carbohydr. Polym., 49: 297-305.