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Influence of Amylopectin Structure and Amylose Content on the Gelling Properties of Five Cultivars of Cassava Starches

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Five cassava genotypes were investigated to identify the fine amylopectin structures and granule chemical compositions, which differentiated the starches into high (T_o = 63.7 °C on average) and low (57.3 °C on average) gelatinization temperatures. The amylose contents (15.9−22.4%) and granular dimensions (12.9−17.2 μm) significantly differed among the starches. Diverse amylopectin structural elements resulted in significant swelling power, viscoelastic properties, and gel firmness. Debranched starches revealed a trimodal amylopectin distribution of three fractions: FIII (DP 12), FII (DP 24.31), and FI (DP 63) and FIII (DP 12), FII (DP 24.69), and FI (DP 67) for the low and high gelatinization starch groups, respectively. The higher proportion of FI long chain entanglement with amylose chain lengths to form longer helical structures was confirmed in the high gelatinization starch group, which developed "true" gels with better shear resistance, frequency independence, and higher gel firmness. Significant amounts of resistant starch fractions revealed the potential for application of these genotype starches in diverse foods.

KEYWORDS: Cassava; debranched starch; amylopectin; swelling power; viscosity; resistant starch

INTRODUCTION

Starch is the most abundant carbohydrate component of cassava and is widely used as a replacement for corn starch in the United States (*1*). Many starch functionalities as stabilizers and physical properties including rheological and viscoelastic characteristics are dependent on two distinct structural polysaccharide fractions—amylose (17−24%) and amylopectin (76−83%) (*1*). Gelatinization and retrogradation are two important physical behaviors of starch that are influenced by these polymer fractions. Gelatinization, manifested by irreversible changes such as swelling, crystallite melting, and starch solubilization (*2*), is the disruption of molecular order within the starch granules when they are heated in water. Retrogradation defines the reassociation of gelatinized starch molecules resulting in more ordered structures. These ordered structures in turn influence starch physical properties such as the viscosity of gels and pastes. Viscosity is largely influenced by the granule shape and swelling power (SP), amylopectin−amylose entanglement, and amylose and amylopectin granular interaction (*3*−*5*). The effects of different mutant genotypes on the proportion of amylose and amylopectin are well-documented (*6*). Therefore, the variations in amylopectin and amylose proportions, structures, and contents would result in starch granules with different chemical and physical properties. One physical property of recent interest is the inclusion of resistant starch (RS) in human diets.

RS, defined as dietary starch that does not digest in the small intestine, behaves like dietary fiber and may have potential as a health-related ingredient in foodstuffs (*7*). Possible beneficial effects of using RS in the diet include lowered pH of the colon, formation of short chain fatty acids in the colon, increased fecal bulk, protection against colon cancer, improved glucose tolerance, and lowered blood lipid levels. This type of RS is starch that retains its natural granular shape yet resists digestion due to crystallinity within the granule (*7*). Hence, specific methods to determine RS are necessary and include direct methods after removing digestible starch (*8*) or indirect methods using the difference between total starch and digestible starch (*9*). In this paper, we adopted (*8*) a direct method with minor modifications. The main features of this procedure involve removal of protein (because protein is a minor component of cassava starch, this step maybe optional), removal of digestible starch and enzymatic hydrolysis of RS, and quantification of RS as glucose released

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× 0.9. The degree of gelatinization influences RS (*8*), and this starch property manifested by starch crystallinity is reportedly (*10*) largely influenced by amylopectin branch chain length distribution; the length of internal chains may determine the degree of local crystallinity (*11*). Amylopectin (a branched polymer) consists of short linear α-1,4 polymer chains linked to each other by α-1,6 linkages. These glycosidic linkages are enzymatically hydrolyzed, using pancreatic α-amylase (*12*), which primarily hydrolyzes α-1,4 linkages.

The structure of amylopectin has been extensively studied by examining the debranched chain profiles using isoamylase (*13*), among others, followed by the separation of linear chains by size exclusion (*14*) or by anion exchange (*15*) and chromatographic methods. Traditionally, differences among cassava varieties were attributed to botanical sources and field growing conditions. Because amylopectin is a principal component of starch, its fine structure has been extensively (*13*, *16*) investigated by enzymic debranching and subsequent high-performance size exclusion chromatography (HPSEC). With this method, a bimodal distribution of chain lengths was found for corn, rice, and potato (*14*, *17*), whereas wheat and tapioca showed a trimodal distribution (*16*, *17*). For analysis of starch chain distributions requiring molecular standards for M_w calibration, low angle laser light scattering (LALLS) and refractive index (RI) detectors connected in-line to HPSEC are widely used (*14*, *16*, *17*). Recently, several authors (*14*, *18*) used multiangle laser light scattering (MALLS) detection in a batch mode and HPSEC with in-line MALLS and RI detectors for the measurement of molecular weights of amylopectins from different origins including waxy maize, normal corn, amylomaize, wrinkled pea, smooth pea, and potato using a MALLS detector (*19*). Unlike the LALLS detector, the measurement using MALLS results in the absolute value of M_w without using standard samples. For the first time, structural analysis of cassava starches amylopectin using the HPSEC with in-line MALLS and RI detectors system connected in series is presented here.

This report is of an ongoing study on some cassava cultivars [Rayong 5, KMUL 36-YOO2 (YOO2), Hanatee, KU50, and Rayong 2] developed in Thailand's cassava breeding program. Previous studies (*20*, *21*) have detailed some of these cultivar starch characteristics and identified differences among the cultivar starch isolates. The objective of this study was to examine the molecular structures of these newly developed cassava starches.

A starch with an altered amylose content and an altered fine structure of amylose and amylopectin would have different functional properties, such as gelatinization temperature, viscoelastic properties, gel strength, SP, and solubility properties. Hence, another objective of this study was to relate the molecular structures of these cultivars with their physical properties. Such detailed information is needed to provide and assist in genetic research of starch biosynthesis and designing starch with tailored properties for food and industrial applications. Moreover, these data would be useful in providing cheaper and alternative economic sources for starch in the developing world.

MATERIALS AND METHODS

Roots were manually harvested, and samples were collected from fields subjected to similar agronomic conditions. Starch extraction was conducted within 12 h of harvest, and the extraction and purification methods followed those described in refs *22* and *23*.

Starch Physical Properties Analyses. The SP and solubility of starch were determined (*24*) with minor modifications. Starch (0.1 g, dry basis) was heated in 40 mL of water to the desired temperature for 30 min. The formation of lumps was prevented by continuous stirring. The mixture was centrifuged at 4000*g* for 15 min, then the supernatant was decanted, and the swollen starch sediment was weighed. The SP was the ratio in weight of the wet sediment to the initial weight of the dry starch. An aliquot of supernatant contained in beakers was evaporated overnight at 80 °C. Following, beakers were further dried at 130 °C for 1 h and then weighed. The solubility was the ratio of weight of the dried supernatant to the initial weight of the dry starch.

To assess the influence of amylose and or amylopectin on SP, the particle size distribution of samples suspended in water was measured. One gram of dry starch was suspended in 10 mL of water at 25 °C and gently stirred for 5 min. The particle size distribution of the suspension was determined using a light-scattering instrument (Mastersizer, Malvern Instruments Ltd., Worcestershire, United Kingdom). The particle size refers to hydrated and suspended particles after mixing with water.

Thermal properties of the starch samples were analyzed using differential scanning calorimetry (DSC) (Micro DSC VII, Setaram, France), bundled with Pyris software. Starch slurries were prepared based on their moisture contents (1:3 starch−water ratio w/v) and were weighed and adjusted in steel cans to a total volume of 0.6 mL. The steel cans containing the starch slurry were hermetically sealed and equilibrated for 1 h and scanned at a heating rate of 1.2°/min from 25 to 115 °C. A sealed can containing equal amounts of water (450 mL) was used as a reference. Gelatinization temperatures (onset, T_o; peak, T_p; and conclusion, T_c) and enthalpy changes (ΔH) were recorded using bundled Pyris software. Viscosity and pasting properties of the starches were determined (*21*) in triplicate by using a rapid viscosity analyzer (RVA, Newport Scientific, Australia).

Gel firmness was carried out following the RVA analyses. The starch slurries were each transferred to a 50 mL beaker, covered, and held overnight at room temperature. Penetration force measurements were made with a TA-TX2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY) fitted with a 10 mm diameter flat-ended cylindrical probe penetrating the gel for a distance of 16 mm at 0.5 mm/s. The peak penetration force was recorded for each gel as *g* force and taken as a measure of firmness.

Small amplitude oscillatory rheological measurements were performed with a Rheostress RS100 (HAAKE, Germany) equipped with parallel plate geometry (20 mm diameter). The gelatinized starch samples were prepared by heating the genotype starches at 85 °C for 5 min and then equilibrating on the rheometer peltier for 5 min. The frequency sweep was performed from 1 to 100 rad/s at 25 °C, 0.5% strain. The storage modulus (G'), loss shear modulus (G''), and loss tan *d* were measured. All measurements were conducted at a frequency of 1.0 Hz and constant stress (0.5 Pa), well within the linear viscoelastic region of starch. Silicone oil was applied to the exposed surfaces of the sample to prevent evaporation throughout the experiment.

The content of RS was determined by a modified enzymatic/colorimetric method (*8*). Samples of 100 mg were treated with pancreatic α-amylase (Sigma A-3176, St. Louis, MO). The residues were extracted after centrifugation for 10 min at full speed, and the supernatants were discarded. The extracted starch was digested with amyloglucosidase (Boerhringer Mannheim 102857) for 48 h at 25 and 37 °C. The color was developed by reaction of the glucose with glucose oxidase and peroxidase (GOD/PAD, Boerhringer Mannheim 676543) for 10 min at 25 °C. The absorbance was measured at 500 nm against blank reagent. A glucose standard solution (5−100 mg/dL) was used to calculate the glucose content. The RS content was measured by calculating glucose release × 0.9 (*8*).

HPSEC-MALLS-RI Analysis. *Molecular Weight Distribution.* The molecular weight distributions of starches were determined by HPSEC (*25*). The solution of native starch was prepared by solubilizing 75 mg (dry basis) of starch with 15 mL of 90% dimethyl sulfoxide (DMSO) solution in a boiling water bath for 1 h with constant stirring and continuousous stirring for 24 h at room temperature. Starch was precipitated from an aliquot of DMSO solution (2.1 mL) with excess absolute ethyl alcohol and centrifuged at 4000*g* for 10 min. The precipitated amorphous starch pellet was resolubilized in deionized water (15 mL, 95 °C) and stirred with a magnetic stirrer in a boiling water bath for 30 min. To the acid−alcohol-modified starch, the starch solution was prepared by solubilizing 10 mg (dry basis) of starch with

Table 1. Chemical Properties of Cassava Genotype Starches[a]

characteristics	Rayong 2	Rayong 5	KU50	Hanatee	YOO2
average granule size (μm)	17.2 ± 0.0	16.4 ± 0.0	14.3 ± 0.2	13.3 ± 0.0	12.9 ± 0.0
amylose content (%)[b,c]	19.5 ± 0.2	17.1 ± 0.0	15.9 ± 0.0	22.4 ± 2.9	20.1 ± 0.0
lipid (%)[c]	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
T_o (°C)[c,d]	59.7 ± 0.1	60.0 ± 0.4	64.4 ± 0.0	63.4a ± 0.3	63.3a ± 0.0
T_p (°C)[c,d]	64.4 ± 0.0	66.8 ± 0.0	69.9 ± 0.0	68.3a ± 0.3	68.2a ± 0.1
T_c (°C)[c,d]	71.6d ± 0.2	72.5d ± 0.4	75.7 ± 0.0	75.0 ± 0.5	74.8 ± 0.1
ΔH (J/g)[c,d]	12.8 ± 0.4	12.9 ± 0.2	13.7 ± 0.0	13.6a ± 0.5	13.6a ± 0.3
RS (% dry matter)	10.5 ± 4.8	13.2 ± 1.4	14.0 ± 0.9	6.8 ± 0.1	8.6 ± 1.6

[a] Values are means ± standard deviation. In the same row, values followed by a common letter are not significantly different at $P < 0.05$, by least significant analysis. [b] Iodine potentiometer titration analysis. [c] Ref *21.* [d] T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH, enthalpy change.

15 mL of deionized water and stirred with a magnetic stirrer in a boiling water bath for 1 h. Each starch solution was filtered through a 5.0 μm syringe filter, and then, the filtrate (100 μL) was injected into an HPSEC system. This system consisted of an HP G1310A isocratic pump (Hewlett-Packard, United States), RI detector (HP 1047A), and a MALLS detector (Dawn DSP, Wyatt Tech., United States) with a helium−neon laser light source ($\lambda = 632$ nm).

The columns used were PWH (guard column), G5000PW, and G4000PW (TSK-Gel, Tosoh, Japan) columns connected in series and kept at 70 °C. The mobile phase was 100 mM phosphate buffer (pH 6.2) containing 0.02% NaN_3 at a flow rate of 0.5 mL/min. The electronic outputs of the RI and MALLS detectors were collected by ASTRA software (ver. 4.50, Wyatt Tech.). Peaks were assigned using the RI chromatograms. The MALLS and RI signals were used to determine the moleculer weight of amylopectin (first peak). Because of the reduced sensitivity of MALLS for small molecular weight species, the molecular weight of the second peak (amylose and degraded amylopectin fragments) of starches was calculated from the RI signal using a calibration curve constructed from a series of pullulan molecular weight standards (peak molecule weight: 5.6, 11.8, 22.9, 46.0, 95.3, 200.0, 359.0, and 769.5 × 10^3 Da; Polymer Standards Service, Uited States).

Chain Length Distribution. Starch solution (2.5 mg starch/2.45 mL H_2O) was prepared according to the procedures described above. The solution was cooled, acetate buffer (0.05 mL, 1.0 M, pH 3.4) and isoamylase solution (10 μL, 5.9 U/μL) were added, and the mixture was incubated in a shaker bath at 45 °C for 24 h (*26*). The solution was neutralized with 0.1 M NaOH and deionized with Amberlite IR-120-P and Amberlite IR-93 (Sigma) ion exchanger. The solution was diluted to 5 mL and heated in a boiling water bath for 10 min. Debranched starch solutions were then filtered using a 0.45 μm syringe filter. The filtrate was injected (100 μL) into the HPSEC system. The system was the same as that used for the determination of molecular weight distribution, except the columns used were (a) G3000PWXL and (b) G2500PWXL (TSK-Gel) connected in series. A typical HPSEC profile of debranched starch showed trimodal distribution. The molecular weight of first peak (amylose) was determined by using MALLS and RI signals, and the molecular weights of the second and third peaks (long chains and short chains of amylopectin) were calculated from the RI signal using a calibration curve constructed from a series of pullulan molecular weight standards (peak moleculer weight: 1.0, 5.6, 11.8, 22.9, and 46.0 × 10^3 Da; Polymer Standards Service). Unit amylopectin chains were classified into three groupings based on the degree of polymerization (DP): 6−12, 13−34, or ≥35 (*27*).

Statistical Analysis. The general linear model and multiple regression analysis (SAS Institute, Cary, NC) were used to analyze the data in triplicate. Correlation analyses between two sets of data were performed using the CORREL analysis tool of Microsoft Excel, which calculates the covariance of the data sets divided by the product of their standard deviations.

RESULTS AND DISCUSSION

Granule Composition and Dimensions. It is apparent that from **Table 1**, the starches have significantly different properties. The mean diameter of isolated starch granules ranged from 13.36 to 17.24 μm (**Table 1**). On the basis of the gelatinization temperatures, the five samples were divided into two groups, low gelatinization temperature starch (Rayong 5 and Rayong 2) and high gelatinization temperature starch (KU50, Hanatee, and YOO2). The lipid content was negligibly low among the starch samples. Within its group, the Rayong 5 larger granule size displayed a lower amylose content (**Table 1**) and corresponding short amylopectin chain lengths and a higher peak viscosity and gelatinization temperatures. Rayong 2 contained smaller granular dimensions and a higher amylose content. Within the high gelatinization temperature starch group, Hanatee and YOO2 had smaller granular dimensions and the highest amylose contents. KU50 had larger granular dimensions, higher gelatinization temperatures (**Table 1**), and the highest proportions of amylopectin molecules and long chain lengths (**Figure 1** and **Tables 2** and **3**). Gelatinization temperatures increased almost linearly with decreasing amylose molecule size and/or content.

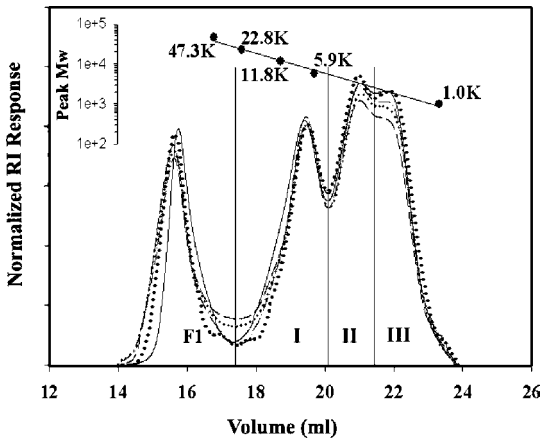

Figure 1. HPSEC of debranched cassava starches Rayong 2 (—), Rayong 5 (• • •), KU50 (–•–•–), Hanatee (—), and YOO2 (■).

Table 2. Weight Average Molecular Weight (M_w) of Amylose Molecules and Debranched Amylopectin Chains Measured with HPSEC-MALLS-RI System[a]

	amylose molecules	debranched amylopectin		
	F1	A (peak 1)	B_1 (peak II)	$B_{>2}$ (peak III)
cultivar[b]	M_w × 105	M_w × 103	M_w × 103	M_w × 103
Rayong 2	2.61 ± 0.4	1.93 ± 0.3	3.93 ± 0.4	10.03 ± 0.2
Rayong 5	2.51 ± 0.2	1.91 ± 0.2	4.02 ± 0.2	10.06 ± 0.1
KU50	2.44 ± 0.2	1.96 + 0.1	4.03 ± 0.1	11.54 ± 0.4
Hanatee	2.70 ± 0.5	1.96 ± 0.4	4.02 ± 0.1	10.00 ± 0.2
YOO2	2.64 + 05	1.98 ± 0.3	3.88 ± 0.2	10.77 ± 0.1

[a] HPSEC, MALLS, and RI. [b] Average of three replicates and means ± standard deviation.

Table 3. Weight Average DP (DP_w) and Relative Mass (%) of Debranched Amylopectin Chain Measured with HPSEC-MALLS-RI System

	chain length distribution[a]						
	DP 6–12	DP 13–34	DP ≥ 35				
	peak 1	peak 2	peak F3	relative mass (%)			A/B mass
cultivar[b]	(A chains)	(B1 chains)	(B2–B4 chains)	peak 1	peak 2	peak 3	ratio
Rayong 2	11.8 ± 2.2	24.6a ± 1.2	62.0a ± 0.2	58.1 ± 2.4	24.9a ± 2.2	17.0 ± 2.2	0.21
Rayong 5	11.7a ± 1.3	24.0 ± 1.2	64.0 ± 1.5	58.2 ± 2.3	24.9a ± 2.7	16.9 ± 0.2	0.20
KU50	12.2 ± 1.1	24.9 ± 1.4	71.3 ± 2.5	57.6 ± 2.2	24.9a ± 2.5	17.5 ± 2.3	0.21
Hanatee	12.1 ± 0.2	24.6a ± 1.1	62.0a ± 2.1	56.7 ± 2.2	25.4 ± 2.3	17.9 ± 0.8	0.22
YOO2	11.7a ± 1.2	24.6a ± 0.8	66.4 ± 2.3	57.9 ± 2.5	24.4 ± 2.4	17.7 ± 1.2	0.22

[a] Sum of peak area ratios (%) of a group with DP. [b] Average of three replicates and means ± standard deviation. Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

Gelatinization and Swelling Properties. To more fully understand the role of amylopectin and amylose molecules in the cassava starches, the starches were solubilized, equilibrated as described above, and investigated by DSC (**Table 1**). It is apparent that the onset (T_o), peak (T_p), and conclusion (T_c) temperatures, on average, for the two low gelatinization temperatures (59.8, 65.6, and 72.1 °C, respectively) are much lower than the four high gelatinization temperature starches (63.7, 68.8, and 75.2 °C, respectively). These data reflect chain length/proportion differences within and between the starch groups and might be used as a basis for further investigating the role of amylopectin fine structures (*27*) on the gelatinization properties of these genotype starches. The significant ($P < 0.05$) differences of T_p (68.2−69.9 °C) of the high gelatinization temperature starch group, as compared to the low gelatinization temperature starch group dissociation endotherms ($T_p = 64.4-66.8$ °C), further elucidates and supports the views (*28, 29*) that amylopectin fine structure and/or crystallites are essentially related to the onset of both SP and gelatinization. Our findings present different amylopectin structures illustrated (**Figure 1**) by the resulting amylopectin chromatograms and are related to differences in terms of extent of double helical structures within crystallization regions (*2*). These starches contain high proportions of double helical material as is evident (*2*) from their higher gelatinization enthalpy (average, 13.6 J g^{-1}) as compared to the low gelatinization starches (average, 12.8 J g^{-1}). These double helices include longer exterior chains representing the prominent FI fractions present in those starches (**Table 2**). Apparently, amylopectin from the high gelatinization temperature cassava starches favors (*30*) the formation of crystalline material, which has higher dissociation temperatures and enthalpies. The presence of long chains (DP > 35) of the high gelatinization temperature starch facilitates crystal formation with longer double helices that are proportionally longer than the low gelatinization temperature starches. This development (i) increases gelatinization temperatures by providing greater restriction to amorphous regions, and as a result of this, (ii) the crystal region hydration increases the gelatinization enthalpy by increasing the amount of longer double helices.

The starch samples contained different amylose contents (**Table 1**), amylopectin structures (**Figure 2** and **Tables 2** and **3**), and displayed different SPs and solubility properties (**Table 4**). Reports on the relationship between SP, amylose content, lipids (*27, 31*), and amylopectin fine structure (*27*) concluded that amylose and lipids inhibited SP and a high proportion of amylopectin long chains (DP > 35 unit chains) resulted in increased swelling. In this report, starch samples within their groups with high proportions of long chains exhibited higher SPs. The SP and corresponding solubility increased linearly with a temperature increase. Within their grouping, the smaller-sized granules of Hanatee and YOO2 displayed a higher SP, whereas the larger granule sizes of KU50 exhibited a lower SP. Similarly, Rayong 5 larger-sized granules exhibited lower SPs and solubilities at all temperatures investigated (**Table 4**). A positive correlation was found between SP and granule size, heated at 80 ($r = 0.96$) and 90 ($r = 0.93$) °C. Granule size did not correlate positively with amylopectin chain distribution, amylose content, and starch gelatinization behavior (*27*) and was also

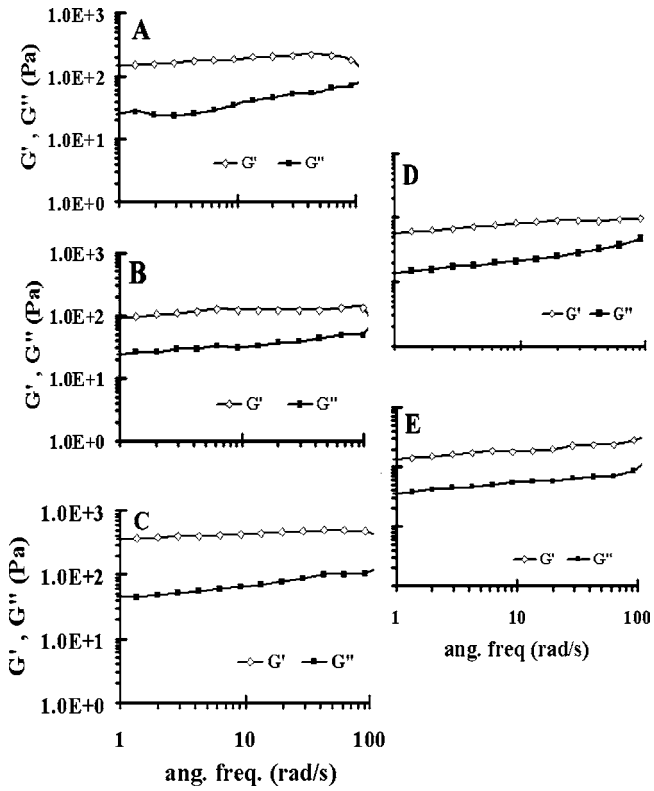

Figure 2. Frequency dependences of dynamic moduli (G and G'') of (**A**) Hanatee, (**B**) YOO2, (**C**) KU50, (**D**) Rayong 2, and (**E**) Rayong 5.

Table 4. Solubility and SP of Cassava Starches[a]

	SP (g/g)[b]		solubility properties (%)	
source	80 °C	90 °C	80 °C	90 °C
Rayong 2	11.9 ± 0.5	30.6 ± 0.7	5.5 ± 0.2	12.7 ± 0.3
Rayong 5	11.8 ± 0.2	27.2 ± 0.3	4.4 ± 0.6	10.6 ± 0.3
KU50	19.1 ± 0.3	36.3 ± 0.2	6.3 ± 0.5	10.9 ± 0.2
Hanatee	19.9 ± 0.5	42.3 ± 1.1	11.8 ± 0.5	20.2 ± 1.5
YOO2	19.5 ± 0.3	40.6 ± 0.8	11.6 ± 0.2	16.2 ± 0.7

[a] Average of three replicates. Values followed by the same letter in the same column are not significantly different ($P < 0.05$). [b] Heating treatments at 80 and 90 °C.

Table 5. Pasting Properties of Cassava Starch Expressed as Percentages of the Full RVA Scale 15 min Test

source[a]	pasting temp	viscosity (%)[b]				
		peak	hot paste	CPV	breakdown	setback
Rayong 2	71.3	94.23	28.45	75.46	55.78	8.77
Rayong 5[b]	71.9	88.88	30.47	79.79	58.41	9.09
KU50[b]	72.4	111.01	25.44	102	85.57	9.01
Hanatee[b]	74.6	142.64	24.66	127.04	117.98	15.6
YOO2[b]	73.4	126.43	30.21	113.13	96.22	13.3

[a] Measurements were performed with a starch sample of 3.50 g (on 14% moisture basis). [b] Ref *21*.

noncorrelative to SP (*27*, *29*) except in recent findings that granule size correlated with SP at 75 °C. Data presented here indicate a similar and new positive correlative relationship between SP and granule size at higher temperatures of 80 and 90 °C. The larger-sized Rayong 5 starch granules as compared with Rayong 2 contained lower proportions of amylopectin long chains (relative mass %, DP ≥ 35 unit chains) (**Table 3**) that were attributed to its lower SP and solubility properties. Suggestions (*27*) that starch swelling is a property of amylopectin supported our findings that Hanatee, YOO2, and Rayong 2, within their groups, contained a higher relative mass of amylopectin long chains (DP ≥ 35 unit chains) (**Table 3**) and exhibited a higher SP (**Table 4**).

Within the two groups, the higher amylose containing starches demonstrated higher SPs and solubility properties. Traditionally, starches (wheat, barley, etc.) (*27*, *28*, *30*, *32*) containing high amylose and lipid contents exhibited low SPs. The presence of an amylose−lipid complex was used to explain the inhibition of SP in these starches. The data here show a new perspective on the relationship between cassava starch SP and amylose content. The low or negligible lipid contents (**Table 1**), hence the consequent lack of an amylose lipid complex in these genotypes starches, might be used to explain this new relationship observed in these starches.

Viscosity and Pasting Properties. The high gelatinization starches had higher pasting temperatures than the low gelatinization starches (**Table 5**) as determined using the RVA. These higher pasting temperatures were attributed in part to the higher amylose contents of the former starch group. Peak (the highest viscosity during heating) and breakdown viscosities appeared to be highest among the starches with higher amylose contents. A greater amount of amylose has conventionally been linked to greater retrogradation tendency in starches (*33*), and this was used to explain the variable cold paste viscosities (at 50 °C) observed among the starches. Conventionally, tapioca starch (*1*), due to the low levels of amylose to reinforce the molecular network within the granules, demonstrated high peak viscosities with consequent great breakdown. During the holding period, the starches underwent considerable shear thinning and/or starch breakdown. The higher gelatinization starches showed (**Table 5**) better shear resistance (hot paste viscosity at 95 °C). KU50, as compared with the starches within its group, had a low amylose content and peak viscosity but high setback viscosities and decreased starch thinning. These findings, however, are not in agreement with conventional theories relating these properties to their chemical properties (amylose content) (*1*, *15*). The peak viscosities of the low gelatinization starches ranged from 84.88 to 88.88% as compared to from 111.01 to 142.64% (**Table 5**) for the high gelatinization starch group. The differences observed in shear thinning among the starches were attributed to their granule sizes (*34*), breakdown and instability of swollen granules caused by high temperature, and shear forces (*35*). Within their respective groups, the swollen granules of Hanatee and Rayong 5 demonstrated increased resistance to shearing and this was attributed to (i) a higher proportion of amylose and amylopectin molecular sizes (**Table 2**) and amylopectin (**Table 3**) long chain lengths leading to (ii) higher interaction between amylose and amylopectin chain lengths (a) increases in SP potential and (b) increases in their peak viscosities. Within its group, Rayong 2 reached the lowest peak viscosity and underwent a relatively greater breakdown probably due to a high amylose content, which holds for normal corn starches (*1*). However, the expected limit in increasing viscosity by the developed aggregated structure (*36*) did not restrict the sample starch's granule swelling and solubility properties (**Table 4**).

Gel Firmness. Firmness as measured by peak puncture force was 20, 12, and 7 *g* for KU50, Hanatee, and YOO2, respectively, and 15 and 5 *g* for Rayong 5 and Rayong 2, respectively. This shows a similar trend to the RVA data, with gel firmness the highest for Rayong 5 and for KU50 within their respective groups.

Dynamic Rheometry. The frequency sweep test was carried out to investigate and characterize the gelling properties of the gelatinized native genotype starches. The starch samples were prepared by heating to 95 °C and then cooled to 25 °C for the frequency sweep. The G' and G'' curves of Hanatee, YOO2, and KU50 were almost parallel in the frequency range of 1−100 rad/s (**Figure 2A**−**C**). Moreover, G' dominated G'' throughout the frequency range examined.

Generally, two classes of networks have been identified (*37*) and referred to as "true gels" and "weak gels". By definition, a true gel is free standing and arises from a three-dimensional network. Within their groups, the cultivars KU50, Hanatee, and YOO2 formed gels that were slightly independent of frequency (*38*, *39*) and, from IPT and HPSEC analyses, contained higher contents of amylose (**Table 1**) (*21*) and amylopectin chain lengths (DP ≥ 35) (**Table 3**) with possibly greater inter- or intraentanglements that would contribute to gel firmness and stability. Rayong 2 and Rayong 5 formed pastes that were dependent on a similar frequency (**Figure 2D**,**E**). This hypothesis is built on the postulation (*21*) that leached amylose increased subsequent interchain associations with exposed exterior amylopectin chains that contributed to increased gel stability.

Starch functionality is largely defined by two structural characteristics: (i) They are composed of amylose and amylopectin, and (ii) a reorganization of these molecules into spherocrystalline granules allows swelling in heated water while maintaining a degree of granular integrity and identity (*1*). The polymers, amylose and amylopectin, demonstrate different rheological properties; for instance, when amylose is released into solution, hydrogen bonds are readily formed (*40*) to produce rigid, opaque gels, a similar behavior observed in the high gelatinization KU50 starch. The amylopectin fraction, however, because of a branched structure, has limited ability toward hydrogen bonding (*40*), and its solutions remain relatively clear and fluid. Rayong 5 and Rayong 2 starch isolates developed gels that demonstrated similar behaviors and were concluded to possess pseudo gel properties (*39*) that were systematically described as pastes (*40*) and/or weak gels. Cooked pastes of Hanatee, Rayong 2, and YOO2 were characteristically clear and soft, whereas KU50 and Rayong 5 formed pastes, which were typically clear to cloudy and formed relatively short opaque gels with a characteristic cassava aroma.

RS. The enzymatic degradation of the starch granules was carried out at 25 and 37 °C, to investigate the effect of

Table 6. Correlation between Starch Properties for Cassava Starches[a]

	amylose	granule size	peak viscosity	breakdown	setback	HPV	pasting temp	RS	T_p	ΔH	SP (80 °C)	SP (90 °C)	DP 6–12%
amylose													
granule size	–0.38												
peak viscosity	0.60*	–0.94											
breakdown	0.59*	–0.92	0.99**										
setback	0.97*	–0.30	0.52*	0.51									
HPV	–0.20	0.35*	–0.52	–0.59	–0.24**								
pasting temp	0.67*	–0.30	0.98**	0.97**	0.55*	–0.47							
RS	–0.99	0.51*	–0.69**	–0.67**	–0.95**	0.18*	0.33**						
T_p	–0.20**	–0.79	0.67*	0.67*	-0.28	–0.47	0.58*	0.05					
ΔH	0.14**	–0.93**	0.86*	0.86*	0.10	–0.55	0.90**	0.44*	0.91**				
SP (80 °C)	0.31	0.96**	0.92**	0.92**	0.28**	–0.56**	0.82**	0.58**	0.83**	0.98**			
SP (90 °C)	0.60*	0.93**	0.95*	0.95*	0.58*	–0.53	0.89*	0.80**	0.60*	0.87*	0.94*		
DP 6–12	–0.58	0.64*	–0.88	–0.88	–0.53	0.84*	–0.85	–0.13*	–0.50*	–0.65*	–0.71	–0.77	
DP ≥35	0.55*	–0.95	0.98**	0.98**	0.51*	–0.57**	0.92**	0.59*	0.68*	0.90**	0.96*	0.99**	–0.82*

[a] ** and * = $P < 0.01$ and 0.05, respectively; $n = 5$.

temperature on the hydrolysis of the starch granules. There was no significant difference observed between the two temperature regimes, and only one set of data (at 25 °C) is reported (**Table 6**). The starch granules (**Table 6**) demonstrated variable granular resistance to enzyme digestion with resistance higher in the high gelatinization temperature starches. This variability was related to their amylopectin unit chain distribution (*10*) and the degree of branching that influences crystallinity (*11*). Starch samples with a higher proportion of long chain lengths (DP > 35) (**Table 3**) were observed to contain a higher amount of RS. These long chains (DP > 35) in starch apparently facilitate crystal formation with longer double helices that increase starch granules to enzymic degradation. This is in agreement with the theory of higher crystalline regions (*11*) in starch granules that increased internal granular order, consequently imparting granular resistance to α-amylase hydrolysis.

Rayong 2 is more soluble (lower resistance to enzyme hydrolysis) due to a higher proportion of branch short chains that resulted in increased dissociation (*1*, *2*) among the amylopectin unit chains and or amylose molecules. Rayong 5 higher distribution of amylopectin long chains resulted in higher heat enthalpies, which indicated the higher crystalline regions in this starch granule. Similarly, in the high gelatinization group, KU50, followed by YOO2 with a higher proportion of long chain lengths (DP ≥ 35) (**Table 3**), demonstrated higher heat enthalpies (**Table 1**) (*2*) and consequently higher RS fractions within their group.

Molecular Properties of Amylose and Debranched Amylopectin. Superimposed trimodal chromatograms from the RI detector obtained from an isoamylase-debranched amylopectin (cassava cultivars) are presented in **Figure 1**. Recovery of the injected mass under the chromatogram was more than 95% for all of the debranched amylopectins. The RI chromatograms of debranched amylopectins (**Figure 1**) showed similar (*14*) trimodal peaks for the amylopectin structures. On the RI chromatogram, a sharp peak, designated F1, was observed before the amylopectin chains eluted and thus indicated the presence of amylose molecules (*14*) in those starch samples. The corresponding mass for the amylose molecules based on the RI response was not negligible but indicated variability in the molecular weights of the amylose molecules among the starches (**Table 2**). Within their groups, the high amylose starches exhibited higher amylose molecular weights and followed a similar trend with the IPT-analyzed amylose content (**Table 1**). The RI curves for debranched amylopectin were divided into three fractions (I, II, and III) as designated on the chromatograms in **Figure 1**, and absolute weight average M_w and relative mass (%) were calculated for the fractions (**Table 3**). Fraction I, with the smallest M_w, consisted of A chains, and fractions II and III represented B1 chains and the larger B chains (B2−B4), respectively (*14*). These three fractions were designated F1 (DP 6−12), F2 (DP 13−34), and F3 (DP ≥ 35) (*27*) (**Table 2**). The peak area ratios of short branch chains A (F1) and short B chains (F2) of Hanatee and YOO2 were slightly lower than those of Rayong 5 and Rayong 2. This meant that these starches were comprised of highly branched amylopectin as compared to those of KU50, Hanatee, and YOO2.

In this study, it is apparent according to the resolution from the columns used that the two low gelatinization starches were comprised of three major populations, with DP_w 11.6−11.8 (F1), DP_w 24.0−24.6 (F2), and DP_w 62.0−64.0 (F3) (**Table 3**). Similarly, the three other high gelatinization starches comprise DP_w 11.7−12.2 (F1), DP_w 24.6−24.9 (F2), and DP_w 62.0−71.3 (F3). The proportion of F2 was on average 16.6% for the two low gelatinization starches but 17.7% for the high gelatinization starches. By comparing the F1 and F2 populations, the F1 proportion was 24.9 and 24.8% for the low and high gelatinization starches, respectively. F2 populations were in higher proportions (58.1%) in the low gelatinization starches as compared with the higher gelatinization starches (57.4%). Hence, in comparison between the groups, the high gelatinization starches contained a higher proportion of long chains (DP ≥ 35) whereas the low gelatinization starches contained a higher proportion of short chains DP 6−12 and DP 13−34, possibly containing a highly branched amylopectin (*1*). The increase in viscosity was more pronounced with the high gelatinization starches than with the low gelatinization starches, which consist of highly branched amylopectin, thus preventing close physical association (*1*) between molecules, which might explain the failure of the development of a rigid aggregate structure in high amylose Rayong 2 starch (**Table 5**) and consequently higher SP and solubility properties (**Table 4**) when compared with Rayong 5. The peak area ratios of the longer chains (DP ≥ 35) correlated positively with SP of the high gelatinization starches at 80 ($r = 0.96$) and at 90 ($r = 0.99$) °C (**Table 6**). The shorter chains (DP 6−12) correlated negatively ($r = -0.65, -0.71$, respectively) with both temperature regimes. This agrees with reports (*27*) that the starches with higher SPs tend to contain higher proportions of amylopectin long chains. This observation is of important consideration, since between the two groups, the higher amylose starches demonstrated higher SPs, however, there was a low to negative correlation between the amylose

contents and the SPs of the starches (**Table 6**). A positive correlation ($r = 0.90$) existed between the peak III (DP ≥ 35) of the starches and heat enthalpies, which elucidates the role and supports the view of amylopectin long chains on gelatinization temperatures (**Table 1**). These long chains reportedly (*2*, *27*) form long double helices that develop longer crystallites that require higher temperatures to dissociate requiring more thermal energy to break the kinetic barrier of these longer crystallites.

Comparison between the two groups of starches revealed that the lower gel temperature starches contained (i) a lower proportion of long branch chains (DP ≥ 35), (ii) a lower amylopectin fraction with a higher proportion of exterior short chains, and (iii) lower proportions of amylose chain lengths (**Table 2**). Structural studies showed that the high gelatinization starches had the longest amylopectin long chain lengths, and it is likely that the long branch chains of that starch group entangled with amylose molecules (*41*) (**Table 2**) more than the long chains of the low gelatinization starch group. From RVA studies, these high gelatinization starches had higher gel consistencies (*21*), hence indicating that the interactions of long branch chains and amylose molecules of these starches functionally increased gelling tendencies and stabilities of these starches.

Amylose interacts with lipids to form a helical complex resulting in strong gel networks (*41*). However, the lipid content in cassava starch was in too small concentrations (*21*) to form any significant complexes with amylose. Hence, (i) the entanglement of the amylose chain lengths with amylopectin longer chain lengths is hypothesized to give rise to these varying gelatinization temperatures, and/or (ii) it is plausible that the short amylopectin branch chains (peaks I and II) form helical complexes with other branch chains to increase starch granular integrity during heating and shearing. This hypothetical explanation of gel stability in those native starches gives rise to cassava or tapioca starches that would not necessarily require chemical modification (traditionally, cross-linking) to produce strong gels with increased shear resistance.

Correlation between the Parameters of Starch Properties. All possible correlations among the 13 parameters of five cassava starch samples are listed in **Table 6**. It is generally accepted that higher amylose content is the major factor contributing to lower peak viscosity and higher setback. For example, previous research indicated that amylose content was negatively correlated with peak viscosity (*42*, *43*). Additionally (*44*), observations of a positive correlation between amylose content and setback for many kinds of sweet potato starch samples were similar to our research in that there was a positive correlation between amylose content and setback ($r = 0.97$). However, a positive correlation between amylose content and peak viscosity ($r = 0.60$) might explain the various pasting properties and swelling potentials of these hybrid starches when compared to the existing conventional theories of starch polymers and starch functionalities. The amylose content correlated positively with pasting temperature ($r = 0.67$), which holds for observations (*44*) of a positive correlation between amylose content and pasting temperature in sweet potato starches. Granule size exhibited a positive correlation with hot paste viscosity ($r = 0.35$), confirming the above relationship that granular dimensions influenced the level of shear thinning sustained by starch granules.

Currently, one of the main factors affecting starch gelatinization properties is the molecular structure of starch. Cassava starches containing high DP ≥ 35 amylopectin chain lengths (**Table 3**) tended to have higher T_p and ΔH starch gelatinization values (**Table 1**) ($r = 0.68$ and $r = 0.90$, respectively) (**Table 6**). Indications (*27*) that starch with lower amylose content exhibited higher values of T_p and ΔH for wheat starch samples agreed with our research, in that negative to low positive correlations between amylose content and two DSC parameters of starch gelatinization, T_p ($r = -0.20$) and ΔH ($r = 0.14$), were also detected in our present data. This low positive relationship might be used to explain the model of amylopectin unit chains interacting with amylose molecules (*41*) resulting in true gel characteristics exhibited in those high gelatinization starches. However, results have been obtained in which the amylose−amylopectin ratio did not affect the DSC parameters of starch gelatinization (*43*). From previous results (*45*), the content of amylopectin short chains was more important than the amylose−amylopectin ratio in accounting for DSC gelatinization properties for sweet potato and buckwheat. Our present data also indicated that the content of amylopectin short chains (DP 6−12) correlated negatively with T_p ($r = -0.50$) and ΔH ($r = -0.65$) in starch gelatinization for five cassava starch samples. However, a significant negative correlation ($r = -0.58$) existed between the amylose content and the content of amylopectin short chains (DP 6−12). Therefore, starch with low amylose content also had a low content of amylopectin short chains and displayed high gelatinization temperatures. The pasting temperature was positively correlated with ΔH in the presence of high long chain lengths DP ≥ 35 ($r = 0.90$). This means that a higher content of DP ≥ 35 would increase the swelling potential of starch, which holds for previous data (*27*) that a higher content of DP ≥ 35 in starch increased the SP of starch. Starch granule resistance linearly decreased with a decrease in DP ≥ 35 chain lengths. Between the two groups, Rayong 2 and Hanatee exhibited a lower distribution of DP ≥ 35 chain lengths and a corresponding lower resistance in the colorimetric/enzymatic test. A positive correlation between starch resistance and DP ≥ 35 ($r = 0.59$) meant that the higher the proportion of DP chains in the starch granule was, the higher the granules' resistance to enzyme hydrolysis. A negative correlation between starch resistance and DP 6−12 ($r = -0.13$) meant that granule resistance decreased with an increase in the proportion of short chains in the starch granules, as was observed in Rayong 2 and Hanatee starches.

In conclusion, it was established that variations between the starches were due to the altered amylose and amylopectin structural elements, e.g., distribution and lengths of short and long chains. The higher gelatinization temperatures exhibited by Hanatee, KU50, and YOO2 starches were attributed to the high interactions among the long branch chain amylopectin and high amylose molecular sizes observed in these starches. This model was used to explain the significant differences in gelling, swelling, gelatinization temperatures, and RS fractions observed among the starches. On the basis of data presented in this paper, these starches would be useful in different food applications. For instance, the low levels of RS fractions in Rayong 2, YOO2, and Hanatee make them suitable for low fiber foods and good feedstock in fermentation processes, whereas KU50 and Rayong 5 would both be useful in high fiber foods and for industrial applications. Differences in these cassava genotype starches present interesting and new areas of researching specific interactions among amylose and amylopectin chain branching networks, helical development and their influence in developing stronger and more stable cassava or tapioca starch gels, and increasing the nutritional potential of this traditionally low nutritious plant food.

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