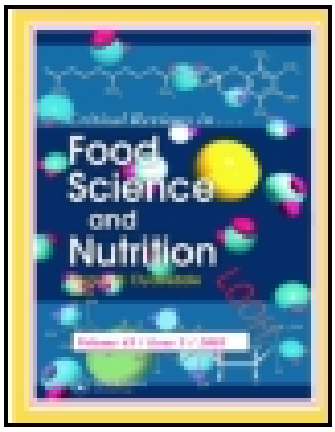

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Structure, Physicochemical Properties, and Applications of Amaranth Starch

Fan Zhu[a]
[a] School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland, New Zealand

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Structure, Physicochemical Properties, and Applications of Amaranth Starch

FAN ZHU *

School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland, New Zealand.

* Correspondence, email: fzhu5@yahoo.com

Abstract

Amaranth as a rediscovered ñnewò crop is surging in the recent two decades. The major carbohydrate of some amaranth species is starch which accounts up to around 60% of the dry grains. This review summarizes the present knowledge of the isolation, composition, structure, physiochemical properties, modifications, and applications of amaranth starches, and provides suggestions for research to further improve the utilization.

Keywords: Amaranth starch, structure, properties, modification, application

INTRODUCTION

Amaranth belongs to genus *Amaranthus* of the family Amaranthaceae in the order Caryophyllales, and consists of around 75 species (Wu, 1998; Cai et al., 2004). It was an ancient crop which was cultivated around 5000ī 7000 years ago in some Mexican regions, but its cultivation was discontinued in the early fifteenth century. Since the late 1970s, grain amaranth was re-discovered and utilized as a ñnewò economic crop (Cai et al, 2004), and has been in local productions of various foods (e.g., amaranth noodles, soy sauce, honey, and biscuits) and animal feeds (Yue et al., 1993; Venskutonis and Kraujalis, 2013). Several species and genotypes of amaranth grain have excellent agronomic traits, such as high biomass potential, high tolerance to drought, salinity, alkalinity, and acidic soils, and exhibit good capacity in adapting diverse biogeographic environments and temperature zones (Yue et al., 1993; Wu, 1998). Thus it has high potential to counteract regional or widespread food shortage, but also malnutrition (Wu, 1998; Venskutonis and Kraujalis, 2013). Amaranth protein scores better than that of many cereals and legumes in terms of the distribution of some essential amino acids (Cai et al., 2004). Compared with most cereal grains, amaranth grains also contain higher levels of oils rich in squalene (Cai et al., 2004). Some amaranth species produce considerable amounts of betacyanin pigments as natural bioactives which may be used as food quality enhancers (Cai et al., 2004). The most abundant component in the grains of some amaranth species is starch (Wu, 1998; Kong, 2009). Whereas many species and genotypes are vegetative or weedy with very low starch yield, the major starch producing seedy species include *A. caudatus*, *A. cruentus*, *A. hybridus*, *A. hypochondriacus*, *A. paniculatus*, and *A. tricolor* (Wu, 1998). In recent years, increasing attention has been focused on the development of amaranth grains as a novel and specialty starch

source. This review summarizes the recent advances in the isolation, structure, physicochemical properties, modification, and applications of amaranth starch from diverse species and genotypes, with an aim to provide a basis for further research and utilization of the amaranth starchy crop in food and non-food industries.

STARCH ISOLATION

Isolation of starch from amaranth seeds/flour poses some difficulties because the fiber and protein can sediment with starch as a brown layer; and some amaranth species contain higher protein level than most cereals. Various methods for the extraction of amaranth starch from seeds have been reported in different studies.

Some earlier method involving dipping the samples in aqueous solution with $HgCl_2$ addition to inhibit the enzyme activity were reported (Wankhede et al., 1989). But the drawback is the potent toxicity of $HgCl_2$ and also a higher amount of protein residues attached to the granules compared with alkaline or acid wet-milling methods reported later.

The most common method is alkali wet-milling employing sodium hydroxide solution (e.g., ~0.25ī 0.1%) (Perez et al., 1993a; Zhao and Whistler, 1994; Mundigler, 1998; Wu and Corke, 1999; Kong et al., 2009a). Briefly, the flour was immersed in NaOH solution for a few hours. The slurry was washed several times by blending with water and centrifugation. Meanwhile, the yellow or brown protein layer on the top of the starch cake was removed. The resulted wet starch cake was dried by either putting it in a heated oven or freeze-drying. Varied methods based on

this wet-milling extraction were developed with claims that improved extraction efficiency or better starch quality could be achieved. A dry-wet milling process involving three-step or five-step abrasive milling in a pearler followed by a short wet-milling was reported (Uriyapongson and Rayasduarte, 1994). Compared with traditional wet-milling, this method gave a higher starch yield and required less time for starch isolation. A combined method of alkaline steeping with low NaOH concentration (0.05%) which is followed by protease treatments was reported (Radosavljevic et al., 1998). The resulted starch contained low residual protein (0.2%) with good recovery. This method was reported to be more economical and has been scaled up to pilot plant level. Another study showed that inclusion of a step with protease addition had little effect on the starch properties (Villarreal et al., 2013).

Resembling corn starch industrial processing, acid wet milling using SO_2 was also reported to isolate amaranth starch and protein with an aim to maintain the quality of protein concentrates (Calzetta Resio et al., 2006; Malinski et al., 2003; Calzetta Resio et al., 2009; Bejarano-Luján and Netto, 2010; Loubes et al., 2012). It was found that the extraction conditions including SO_2 concentration and soaking temperature had a great influence on the starch properties (Loubes et al., 2012). The advantage and disadvantage of alkali and acid milling for specific purposes remains to be established systematically.

Other less used methods are also reported. Al-Hakkak and Al-Hakkak (2007) described a novel non-destructive and non-toxic method by adding extraneous wheat gluten into the flour with sodium chloride to bind the plant proteins, thereby reducing their solubility in water and separating starch from the coherent protein mass. Microfiltration was also attempted to extract

starch from amaranth starch-milk produced by the pilot-scale process (Middlewood and Carson, 2012a, b), though the protein content of the starch fraction was high compared with other methods and the membrane needed to be effectively cleaned afterwards.

STARCH YIELD AND CHEMICAL COMPOSITION

The starch yield, amylose, total lipid, and protein contents of amaranth starches from diverse species in different studies over the last five decades have been reported to be in the range of 2.0ï 65.2%, 0.0ï 34.3%, 0ï 1.8% and 0.02ï 0.98%, respectively (Table 1). The species with higher starch yields (~ > 10%) are *A. hypochondriacus*, *A. cruentus* (synonym: *A. paniculatus*), and *A. hypochondriacus* x *A. hybridus*. The crude lipid and protein contents in the starch granules appear mainly dependent on the specific isolation methods as described in the last section, and may be reduced to a minimum using desired extraction procedure. Trace amount of phosphorous (0.008%) was also reported in amaranth starch as measured by ^{31}P-nuclear magnetic resonance spectroscopy (Lim et al., 1994). The amylose contents of amaranth starches from most species tend to be lower than that of normal cereal starches, though some genotype/species (e.g., *A. retroflexus*) exhibited amylose contents of ~34.3% which is higher than most normal cereal starches. The genetic variation in amylose contents of amaranth starches may provide excellent opportunities to diversify the properties for different applications (Wu and Corke, 1999; Kong et al., 2009a). It should also be noted that the variation in amylose content of different studies may be partially attributed to the specific measuring method used (e.g., concanavalin A precipitation

vs iodine binding *vs* size-exclusion chromatography with or without debranching) (Zhu et al., 2011a).

GRANULE MORPHOLOGY

The granules of amaranth starches from diverse species are mostly polygonal with a size in the range of 0.5ī 2 ε m (Table 2). Amaranth starch is in general smaller than that of cereals and tubers and roots (Singh et al., 2003; Hoover et al., 2010), and is comparable to that of *Arabidopsis* leaf starches (Smith, 2012). The small size of amaranth starch renders it unique properties for various applications. The genetic basis of the granule size and shape is still not fully understood.

POLYMORPHIC PATTERN AND CRYSTALLINITY

The external chains of amylopectin inside the starch granules are crystallized and packed into A-, B-, or C-type as revealed by wide-angle X-ray diffraction (Imberty et al., 1991). Like most cereal starches, all the amaranth starches analyzed so far showed an A-type pattern (Table 3). This may be attributed to the shorter distance between branches in the clusters of amylopectin (IB-CL) within the amorphous region of granules compared with that of B-type starch (Bertoft, 2013). The crystallinity of amaranth starch from diverse genotypes and species ranged from 24.5ī 27.9% (Kong et al., 2010). Another study reported a value of 45.5% for one genotype of *A. cruentus*

(Qian and Kuhn, 1999). The methods of calculating the crystallinity in different studies should be carefully compared (Lopez-Rubio et al., 2008).

MOLECULAR STRUCTURE OF AMYLOSE AND AMYLOPECTTIN

Starch is consisted of two major types of biopolymers of anhydroglucose units: the linear amylose elongated by Ŭ-1,4 bonds and amylopectin branched through Ŭ-1,6 bonds. Branched amylose is also reported. Little is known about the amylose structure of amaranth starch. One study showed that the ɓ-limit value (ɓ-LV (%)) of isolated amylose from *A. paniculatus* as 88% (Wankhede et al., 1989), suggesting the branches exist in amylose molecules. Amylose content has been linked to the physical properties of amaranth starch (Wu and Corke, 1999; Kong et al., 2009a). The molecular size of amaranth amylose and its branching pattern remain to be explored.

The major component in amaranth starch is the branched amylopectin. Depending on the dissolving and instrumental conditions, the molecular weight of amaranth amylopectins from *A. hybridus* x *A. hypochondriacus* and *A. hypochondriacus* has been shown to vary from ~1 to 70 × 10^7, as revealed by diverse light scattering techniques (Bello-Pérez et al., 1998; Wilhelm et al., 2002). Each granule on average consists of around 1700 amylopectin molecules (Wilhelm et al., 2002). The external chains of amylopectin are believed to form double helices and contribute to the formation of the crystalline part in the granules, whereas the internal chains contribute to the formation of branches and the amorphous regions (Pérez and Bertoft, 2010; Bertoft, 2013). The molecular structure of amylopectin and its internal part (segments between the reducing end and outmost branches) from diverse genotype and different species are reported (Table 4). The unit

chain length distribution of amylopectin revealed by high-performance anion exchange chromatography (HPAEC) after debranching can be categorized into four factions (fa, fb1, fb2, and fb2) (Hanashiro et al., 1996), and has been related to the functional properties of amaranth starch (e.g., gelatinization and pasting) (Kong et al., 2008; Kong et al., 2010). Genetic diversity in unit chain length distribution of amaranth amylopectin was reported (Konishi et al., 1985; Kong et al., 2008). The average chain length (CL) ranged from 17.4 to 18.2. The profile fits within the range of A-type starches (Hanashiro et al., 1996; Kong et al., 2008). The external chains of amylopectin can be removed by exo-acting enzymes such as phosphorylase *a* and/or ɓ-amylase to obtain the ű,ɓ- or ɓ-limit dextrins (LDs) (Pérez & Bertoft, 2010). In the form of ű,ɓ-LDs, all of the A-chain (chains that carry only one chain) appear as maltose stubs, whereas the rest, other than maltose stubs, are B-chain (chains that carry more than one chain). The molecular structure of ű,ɓ-LDs can be analyzed by HPAEC after debranching by pullulanase and isoamylase to obtain the chain length distribution. The molar amount of A-chains in amaranth amylopectins ranged from 51.8 to 54.5%, and the ű,ɓ-LV (%) from 53.9ī 56.8%. The average external chain length (ECL) and internal chain length (ICL) were 10.9ī 11.9 and 5.2ī 5.6, respectively (Kong et al., 2008). Based on the internal structure profile, amylopectins from diverse botanical origins were categorized into four groups (Bertoft et al., 2008). Group 1 has the greatest amounts of shorter B-chains (~degree of polymerization (DP) < 30) and least longer B-chains (~DP > 30), whereas group 4 has the opposite trend. Group 2 and 3 fall in between groups 1 and 4 (Bertoft et al., 2008). The internal molecular profile of amaranth amylopectin thus fits into the features of group 2.

CLUSTER STRUCTURE OF AMYLOPECTIN

The branches are located in the internal part of amylopectin and are believed to be arranged in ñclusterò fashion (Bertoft, 2013). The clusters in amylopectin can be isolated by partial hydrolysis with Ŭ-amylase of *Bacillus amyloliquefaciens*. The Ŭ-dextrins of clusters can be further subjected to phosphorylase *a* and/or ɓ-amylase to obtain the ű,ɓ- or ɓ-LDs of clusters so that cluster structure from diverse origins can be compared and characterized by diverse chromatographic techniques before and after debranching (e.g., gel-permeation chromatography (GPC) and HPAEC) (Pérez and Bertoft, 2010). So far only one study has been conducted on the characterization of cluster structure of amaranth amylopectin from two genotypes of *A. cruentus* (Table 5) (Kong et al., 2009b). Amaranth clusters have an average DP of 57 with around 49.2ī 50.1% (molar basis) a-chains and around 8.8ī 9.1 chains per cluster by number (NC). The inter-cluster chain length (IC-CL), describing the distance between each cluster within a group of clusters (domain), is 13.8 glucose residues.

The clusters from amylopectin can be further subjected to extensive hydrolysis with Ŭ-amylase of *B. amyloliquefaciens* to isolate tightly branched building blocks which are practically Ŭ-limit dextrins (Ŭ-LDs). The structure of building blocks can be characterized by diverse chromatographic techniques (GPC and HPAEC) before and after debranching. Amaranth amylopectin contains around 6.0ī 6.1 block per each cluster by number (NBbl). The distance between each branch within a cluster (IB-CL) is 6.8 glucose residues. The branched building blocks can be categorized into five groups (2ī 6) according to the number of chains per each block (Pérez and Bertoft, 2010). Based on the average structural parameters, an amaranth cluster

in the form of ű,ƃ-LD may be visualized (Pérez and Bertoft, 2010) (Figure 1). The cluster in the model consists of six building blocks, one longer b2-chain, linking three blocks, was possibly formed by the Ŭ-amylolysis when the cluster was produced, and the rest are b1-, b0- and a-chains. The b1-chain links two blocks and b0-chain participates in the formation of the block, whereas a-chains carry only one other chain (Pérez and Bertoft, 2010).

The cluster molecular structure has been linked to the thermal properties of starch (Vamadevan et al., 2013). It was shown that onset gelatinization temperature (T_o) negatively correlates with number of building blocks per cluster (NBbl) and positively correlates with inter-block chain length (IB-CL). Thus the diversity in physicochemical properties of amaranth starches (Tables 6ī 11) may reflect in the structural variation in the amylopectin clusters. Thus it would be interesting to explore how the cluster structure may contribute to the formation of these small-sized amaranth granules.

GELATINIZATION MEASURED BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

In the presence of excess water upon heating, starch undergoes a phase transition with the water penetrating into granules, swelling of granules, and the loss of crystalline order. This phenomenon can be monitored with a range of instruments while differential scanning calorimetry (DSC) is one of the most used. The transition temperatures, T_o (onset), T_p (peak), and T_c (conclusion), and also the enthalpy (ϕ*H*) were mostly recorded (Table 6). Most of the previous studies employed a heating rate of 10 ^oC/min and a starch: water ratio of 1:3 (w/w) which ensure the full gelatinization of the amaranth starch granules (Calzetta Resio and Suárez, 2001) and enables a direct comparison of data from different studies. There is great genetic

diversity in the gelatinization properties of amaranth starches between different species (Wu and Corke, 1999; Kong et al., 2009a) (e.g., T_o = ~60ī 73 ^oC), whereas among the same species, genetic variations were also observed (Kong et al., 2009a). Thus it may be concluded that DSC gelatinization parameters do not represent the species in *Amaranthus*, or the botanical origins of starch type (Singh et al., 2003). It may also be concluded that the size of the granules are not related to the gelatinization behavior when the amaranth data is compared with that of other starches (Singh et al., 2003).

With excess amount of water present, the gelatinization of starch is mostly affected by amylose content and amylopectin molecular structure on the molecular level (Zhu et al., 2011b). The molecular structure of the internal part of amylopectin, which forms its backbone, is related to the gelatinization parameters which to a large extent may be controlled by the distance between the branches (IB-CL) (Vamadevan et al., 2013). Indeed, correlation analysis showed that the internal molecular structure is closely related to the DSC results of amaranth starches (Kong et al., 2008).

SWELLING AND SOLUBILITY

During gelatinization, the granules swell and the granular architecture is disrupted while the starch components leach out and are greatly solubilised. The swelling and solubilisation pattern during heating reflect the location of amylose and amylopectin within the granules and their relative contribution to the packing of crystalline and amorphous parts. On the molecular level, they are affected by the ratio of amylose to amylopectin and also their molecular structures (Hoover, 2001). The degree of granule swelling is usually quantified as swelling power (SP) or

swelling factor (SF). The former relates to the inter- and intra-granular water whereas the latter reflects solely intra-granular water (Tester and Morrison, 1990; Hoover et al., 2010). SP was mostly reported for the amaranth starches (Table 7). Starch components in the form of amylose and also smaller amounts of amylopectin leached out during swelling are usually quantified as solubility (%) (S) or water soluble index (%) (WSI).

Great genetic diversity in swelling properties as reflected by the variations in SP, SF, S, and WSI was observed between different species and also in different genotypes of the same species. Correlation analysis of amaranth starches from 15 genotypes within 5 species showed that WSI (85 ^{o}C) is highly related to the amylose content (Kong et al., 2009a), whereas SP and WSI had little correlation with amylopectin molecular structure (Kong et al., 2008). Thus the granular architecture may be critical to the swelling data. Compared with tuber and root starches (Li and Yeh, 2001), amaranth starches have lower SP generally. It was shown that granular size was positively related to the SP of starches from different botanical sources (Li and Yeh, 2001). Indeed, amaranth starch has much smaller granular size than most of other starches. The phosphate groups in some tuber and root starches also facilitate the swelling by pushing the chains away from each other through the Coulomb force repulsion (Hoover, 2001), and amaranth starch contains very little phosphorous. Amaranth starches have comparable SP compared with pulse starches (Hoover et al., 2010). SP of amaranth starch tends to peak around 60ī 70 ^{o}C before dropping towards 90 ^{o}C with larger amounts of materials solubilised (Kong, 2009a), which differs from the pattern of pulse starches. This may be attributed to the higher amylose contents in pulse starches, contributing to the stability of the granules (Li and Yeh, 2001; Hoover et al., 2010). Compared with most cereals, amaranth starch in general has a different swelling pattern.

Apart from amylose content and granular morphology, the lipids in cereals in the form of amylose-lipid complex were shown to inhibit the swelling (Tester and Morrison, 1990).

RHEOLOGICAL PROPERTIES

Pasting refers to the physical changes in starch with water upon heating in the presence of constant shear forces, including swelling of granules, leaching of specific components, and viscosity changes (Hoover et al., 2010). The Rapid Visco-Analyzer (RVA) and Brabender Viscoamylograph (BVA) are most commonly used to measure the pasting properties of amaranth starches (Table 8). Paste with higher starch concentration has higher viscosity, thus the starch content of the test samples should be noted for the purpose of possible comparison between different studies. Compared with starches from normal cereals, pulses, tuber and roots (Wu and Corke, 1999; Hoover, 2001, Hoover et al., 2010), amaranth starches tend to have lower viscosity, lower breakdown and setback with a more stable paste in general, and may be to a large extent due to their small granular size and also their lower amylose contents. Great diversity in pasting properties, as reflected by pasting temperature, peak viscosity, breakdown, and setback, was observed between different species and also in different genotypes of the same species from different studies. Correlation analysis of amaranth starches from 124 genotypes within 9 species (Wu and Corke, 1999) and also from 15 genotypes within 5 species (Kong et al., 2009a) showed amylose content was positively related to the viscosity of the paste and also the setback measured by RVA. Shorter chains in amylopectin (e.g., fa fraction (DP 6ī 12)) and its internal

parts (e.g., B1b (DP 18ï 22)) were related to lower viscosity, whereas longer chains (e.g., fb3 (DP Ó37) in amylopectin and B3 (DP Ó53) in its internal part) were linked to higher viscosity.

While pasting analysis by RVA or BVA is one of the most common rheological tests for amaranth starch, some other types of rheological tests such as dynamic measurements were also reported (Wu, 1998; Wilhelm et al., 2002; Teli et al., 2007; Kong et al., 2010). The storage modulus (G') is an indicator of the energy stored in the material and recovered from it per cycle, whereas the loss modulus (G'') represents the energy dissipated or lost per cycle of sinusoidal deformation. The ratio of the energy lost to the energy stored for each cycle can be defined by tan ŭ (= G''/G') as an alternative parameter indicating the physical behavior of the system (Ferry, 1980). RVA/BVA tests and dynamic rheological measurements are intrinsically linked as revealed by correlation analysis between different parameters (Wu, 1998). Rheological diversity was observed between different amaranth genotypes (Wu, 1998; Kong et al., 2010). High G' and G'' were related to higher amylose content with more solid-like gel (Kong et al., 2010). Higher amounts of fa (DP 6ï 12) and lower amounts of fb1 (DP 13ï 24) and fb2 (DP 25ï 36) were related to lower temperature where the G' reached a maximum during heating (Kong et al., 2010).

GELLING PROPERTIES

Gelling properties of starch paste formed in the canister from RVA pasting analysis can be texturally characterized. The starch paste can be put at 4 ^{o}C for 1 day to undergo retrogradation and gelling. The texture of the resulted gel was measured by Texture Profile Analysis (TPA) to obtain the hardness and adhesiveness (Table 9). The initial firmness of the gel may be mostly

attributed to the formation of amylose matrix and the subsequent slow increase in gel hardness to the recrystallization of amylopectin (Morris, 1990). Adhesiveness is more of a surface property and depends on a combined effect of adhesive and cohesive forces, and other factors such as viscoelasticity (Adhikari et al., 2001). Great diversity in gelling properties as reflected by hardness and adhesiveness was observed between different species and also in different genotypes of the same species in two separate studies (Wu and Corke, 1999; Kong et al., 2009a). Compared with most starches from cereals and root and tubers (Wu and Corke, 1999; Gunaratne and Corke, 2007), amaranth starches tend to have softer gels with higher adhesiveness. The gel properties are related to the characteristics of amylose matrix, the deformed granules as the fillers in the matrix, and the physicochemical interactions between the matrix and fillers (Morris, 1990). The weak gelling properties of amaranth starches may be to a large extent attributed to their low amylose contents. The amaranth starches with comparable amylose contents to some cereal starches had higher adhesiveness (Wu and Corke, 1999). Thus it appears the amylopectin component also contributes to the adhesive properties of gelling.

RETROGRADATION

Upon cooling, the amylose and amylopectin molecules in the gelatinized starch interact with water and each other to retrograde and re-crystallize to form a more ordered structure. Retrogradation is associated with the increase in crystallinity degree, gel firming, and syneresis, and can be quantified by various methods such as rheometry, DSC, wide angle X-ray diffraction, nuclear magnetic resonance, and turbidimetry to reflect different aspects of this phenomenon

(Hoover, 1995). The retrogradation properties of amaranth starch were commonly measured by DSC and are summarized (Table 10). The water content, storage temperature and time, and also the molecular structure of starch components have profound effects on the retrogradation behavior. It was found that amaranth starch gels had better resistance to retrogradation at 25, 4, and ï 20 °C storage temperatures than did corn, wheat, or rice starch gels (Baker and Rayas-Duarte, 1998b). This may be attributed to the low amylose content in amaranth starches. Another study monitoring the textural changes in gel hardness over a period of 7 days at 4 ^{o}C from 124 amaranth genotypes showed that some genotypes may retrograde faster than selected cereal starches (Wu and Corke, 1999). It should be noted that the nature of this textural method in measuring starch retrogradation differs greatly from that by DSC (Zhu et al., 2011a).

FREEZE-THAW STABILITY

Freeze-thaw stability of foods is required in many processing and storage scenarios where several freeze-thaw cycles cannot be avoided. This stability can be quantified through centrifugation by the amount of water separated from a gel after freezing and thawing has occurred, and also by DSC (Baker and Rayas-Duarte, 1998a). Studies showed that amaranth starch tends to have excellent freeze-thaw stability compared to corn, wheat, and rice starches, through several freeze-thawing cycles (Sudhakar et al., 1992; Baker and Rayas-Duarte, 1998a; Bello-Pérez et al., 1998). Thus amaranth starch may be an alternative to some chemically modified starches to ensure freeze-thaw stability of some foods through moisture management.

IN VITRO α-AMYLOLYSIS OF GELATINIZED AND GRANUAR STARCH

In vitro Ŭ-amylolysis of gelatinized or granular starch may provide a clue on the *in vivo* nutritional properties of starch-rich foods or feeds. It may also provide structural information of the granules. The susceptibility of amaranth starch to various enzymes including glucoamylase, human salivary Ŭ-amylase, and porcine pancreatic Ŭ-amylase has been reported (Table 11). In general, both in the granular and gelatinized forms, amaranth starches have higher enzyme susceptibility compared with other starches from most cereals, pulses, tuber and roots (Konishi et al., 1985; Yanez et al., 1986; Capriles et al., 2008; Bello-Pérez and Paredes-López, 2009; Hoover et al., 2010). For example, amaranth starch granules were digested by glucoamylase about 7~10 times faster within the first hour than that of normal maize (Konishi et al., 1985). Hydrostatic pressure treatments failed to increase the resistant starch content in amaranth starch but in wheat and quinoa starches (Linsberger-Martin et al., 2012). This may be due to the smaller granule size, and also to the lower amylose contents in amaranth starches since it is known that high amylose content is usually associated with high resistance to enzymatic hydrolysis (Svihus et al., 2005; Hoover et al., 2010). For granular starch, an inside-out layer-by-layer digestion pattern was observed for some cereal granules (Zhang and Hamaker, 2006). It would be interesting to know the pattern for the amaranth starch with so small a granule size.

MODIFICATION

Native starch can be modified enzymatically, chemically, and/or physically to diversify its functional properties to suit diverse applications. Various chemical and/or physical modifications

have been applied on amaranth starches mainly from three species (*A. cruentus*, *A. hypochondriacus*, and *A. paniculatas*) (Table 12).

Chemical modification

Substitution

The hydroxyl groups in starch molecules can be substituted with a range of hydrophobic and/or hydrophilic functional groups to achieve novel and unique functional properties for applications in food and non-food industries (Table 12). Because of the small size of amaranth granules, the conditions for the synthesis of substituted starch with desired degree of substitution usually differs between amaranth and other sources.

Hydroxypropylation

Hydroxypropylated starch can be prepared by treating starch with propylene oxide in alkali solution. Hydroxypropyl derivatives of waxy amaranth starch from *A. cruentus* with varying degree of molar substitution (Pal et al., 2000) with improved freeze-thaw stability were prepared (Pal et al., 2002).

Succinylation

Succinylated starch can be prepared by treating starch with succinic anhydride in the presence of pyridine. Conditions for preparing the succinate derivatives of waxy amaranth starch from *A. paniculatas* were optimized in terms of the molar substitution degree (Bhandari and Singhal, 2002a). Increased degree of substitution (0.05ī 0.2) was accompanied with decreased gelatinization temperature and peak viscosity. The succinylated amaranth starch showed good freeze-thaw stability (Bhandari and Singhal, 2002b).

Octenyl succinylation

Octenyl succinylated starch can be prepared by treating starch with *n*-octenyl succinic anhydride in alkali solution. Conditions for preparing the octenyl succinyl derivatives of amaranth starch from *A. paniculatas* were optimized to achieve a molar substitution degree of 0.02 (Bhosale and Singhal, 2006). Octenyl succinylation of amaranth starch increased the swelling power and peak viscosity during pasting and also freeze-thaw stability and emulsification capacity, decreased the gelatinization temperatures and enthalpy, and had little effect on the X-ray diffraction pattern (Bhosale and Singhal, 2007).

Carboxymethylation

Carboxymethylated starch was prepared with amaranth starch from *A. paniculatas* with the carboxymethylating agent sodium nonchloroacetate in an alkali environment (Bhattacharyya et al., 1995a). The carboxymethylated starch had improved freeze-thaw stability and increased

viscosities during pasting. However, with increasing degree of substitution in the range of 0.1ī 0.2, the pasting viscosity decreased (Bhattacharyya et al., 1995b).

Phosphorylation

Phosphorylated starch can be prepared by treating starch with sodium tripolyphosphate and sodium trimetaphosphate in alkali condition. Phosphorylated amaranth starch from *A. cruentus* was prepared and applied in a low fat mayonnaise system (Hanson, 1998).

Cross-linking

Cross-linked starch can be prepared in an alkaline solution by treating the granules with cross-linking agents such as sodium tripolyphosphate. Cross-linking starches from *A. cruentus* and *A. hypochondriacus* increased gelatinization temperature range and gel consistency, but decreased resistance to mechanical breakdown, blue value, and initial pasting temperature. Modification effects were greater for starch from *A. hypochondriacus* than from *A. cruentus* (Perez et al., 1993b). Another study showed the cross-linked starch from *A. cruentus* decreased the swelling power and also breakdown viscosity during pasting, and increased the gel hardness (Gunaratne and Corke, 2007).

Acid hydrolysis

Acid-modification of starch has important applications in production of gum and candies, fat replacers, textiles, paper, and pharmaceutical ingredients (Kong et al., 2012). Amaranth starches varying in amylose contents from five genotypes of *A. cruentus* and *A. hypochondriacus* were treated with HCl (0.5 M) up to 12 h. Gelatinization temperatures (T_o, T_p, and T_c) and enthalpy (ΔH) decreased steeply initially, and had an increase with further treatment before it decreased again. With increased amylose content, the effects of acid hydrolysis on gelatinization temperatures became less pronounced. Prolonged acid hydrolysis decreased the storage (G') and loss moduli (G'') revealed by rheological studies, with the starch pastes becoming more liquid-like (Kong et al., 2012). Acid-modification of amaranth starch with higher acid concentration (e.g., 2.2 M) remains to be studied.

Oxidation

Oxidization of starch can be achieved using sodium hypochlorite (NaClO). Optimization of conditions for the synthesis of oxidized amaranth starch from *A. paniculatas* was conducted for the purpose of developing gum arabic substitute for encapsulation of flavors (Chattopadhyay et al., 1997 and 1998). The results suggested similar encapsulation efficiency between arabic gum and oxidized amaranth starch which is also free from hygroscopicity (Chattopadhyay et al., 1998).

Physical modification

Heat-moisture treatment (HMT)

Heat-moisture treatment (HMT) can facilitate starch chain interactions within the amorphous and crystalline domains, thus improving the structural defects in the granules (Hoover, 2010). It is usually conducted at a temperature range of ~100ī 130 ^{o}C with a moisture content of less than 35%. Treating amaranth starch from *A. cruentus* with low moisture level (30%) and high temperature (100 ^{o}C) decreased the swelling factor and amylose leaching, and increased the gelatinization temperature and pasting viscosities (Gunaratne and Corke, 2007).

Annealing (ANN)

Annealing (ANN) refers to the hydro-thermal treatment of starch with the water content of ~40ī 65% at the temperature below the onset of gelatinization (Hoover et al., 2010). Like HMT, ANN can also lead to interactions and re-arrangements of unit chains within the amorphous and crystalline regions, thus improving the structural defects in the granules. Annealing amaranth starch from *A. hypochondriacus* at a range of temperature (~25ī 65 ^{o}C) increased the onset (T_o) and peak temperature (T_p) but had little effect on conclusion temperature (T_c) (Paredes-López and Hernádez-López, 1991).

λ-Irradiation

ɔ-Irradiation can be effective in the inactivation of microorganisms, and it has proven successful in ensuring the safety and extending the shelf life of foods. It can also be used in starch

modification to diversify its functionalities (Kong et al., 2009c). Two amaranth starches from *A. hypochondriacus* and *A. paniculatus* were ɔ-irradiated at 2, 4, 6, 8, and 10 kGy. The results showed that ɔ-irradiation decreased the pasting viscosities, and also the storage (G') and loss moduli (G'') of rheological properties, and had little effect on the gelatinization parameters measured by DSC (Kong et al., 2009c).

High-hydrostatic pressure

High-hydrostatic pressure technology has advantages over heat treatment like better retention of nutritional and functional ingredients in the processed foods. High pressure also may produce foods with novel texture (Vallons and Arendt, 2009). It was found that high-hydrostatic pressure increased the granular swelling but had little influence on the resistant starch formation in waxy amaranth starch from *A. cruentus* (Linsberger-Martin et al., 2012). Thus it would be interesting to test other amaranth starches with higher amylose content.

Applications

The very small granule size and usually low amylose content make amaranth starch unique for some food and non-food applications such as fat replacers, manufacturing biomaterials with novel properties, and carrier and encapsulation materials (Table 13).

For food applications, the native starches were used as composite flour ingredients for fried snacks to reduce the oil uptake (Ahamed et al., 1997); and as fat replacer up to 50% in frozen

desserts (Malinski et al., 2003). In the modified forms, phosphorylated starch was used in mayonnaise as fat replacer (Hanson, 1998); and hydroxypropylated and oxidized starches were used in flavor encapsulation (Chattopadhyay et al., 1998; Kshirsagar and Singhal, 2008). For non-food applications, the native starches were used as functional and/or cheap ingredients in the formation of low-density films (Ahamed et al., 1996), thermoplastics (Wilhelm et al., 1998), super-absorbents (Teli and Waghmare,2010), and dye thickeners in textiles (Teli et al., 1996; Teli et al., 2007 and 2009). The use of amaranth starch in diverse food/non-food systems can reduce the production cost and/or impart the products with novel/desired properties.

Amaranth starch may be suitable agents for moisture management where freeze-thaw cycles exist, possible substrates to efficiently make smaller particles (e.g, nanoparticles) for novel biomaterials, ingredients for specialty snacks and novel emulsification systems, and carriers in cosmetics production. The applications of amaranth starch in food and non-food industries remain to be further explored.

CONCLUSION AND OUTLOOK

A century ago, the ultra-small starch granules from the *Amaranthus* were already observed (Reichert, 1913). The literature from the last five decades showed that the unique properties make amaranth starch a good candidate for various applications. In a majority of the reports, these functionalities include, but were not limited to, the following: (1) Ultra-small granule size (~1 ε m) with A-type X-ray diffraction pattern; (2) Small cluster size with around 9 chains and 6 building blocks per each cluster by number; (3) Low amylose contents with many of the studied

samples being waxy; (4) Easy to swell with low swelling power and good solubility; (5) Low gelling and retrogradation; (6) Good freeze-thaw stability; (7) High susceptibility of raw and gelatinized starches to the attack of Ŭ-amylases.

Natural variations (due to genetic and environmental factors) in the properties showed that some genetic resources could be better utilized to expand the range of applications. Physical and chemical modifications further greatly contributed to the variation in the functionalities, thus expanding their utilizations. To further explore the value of amaranth starch to better suit diverse food and industrial applications, further fundamental and applied studies are needed in the following areas:

To widen the natural variations in the properties of starch, further genetic resources can be accessed to discover genotypes with novel properties; breeders can develop novel starches of smaller granules and/or higher amylose content; environmental factors can also be accessed for local development of the amaranth crop with higher starch yield.

To better understand the starch structure, opportunities exist in the following aspects: structure of amylose; unit chain length distribution of the C-chains with the reducing end; structural changes during seed development; observation of the blocklet structure using atomic force microscopy (AFM); structural contribution of the amylopectin clusters to the formation of small granule size; comparative analysis with *Arabidopsis* leaf starch which is B-type but with similar ultra-small granular size to reveal the molecular basis of the type of starch crystallinity; and enzymatic and/or hydrothermal treatments to further reveal the granular structure. The longer term goals for structural elucidation may include isolation and characterization of blocklet; revealing to what

extent the longer chains in amylopectin participate in the formation of crystalline lamella in the granules; the location of amylose in the granules; and how many molecules per each granule by number there are.

Physical and chemical modifications have been limited on too few genotypes. To widen the ñun-naturalò variations in properties achieved by modification, more genotypes varying in structural features and amylose content can be tested. Combinations of physical, chemical, and/or enzymatic modifications may achieve greater diversity in functionalities. In turn, the newly developed starches with novel functionalities may be further explored for diverse applications.

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Table 1 Starch yield and chemical composition

Species	No.	Yield (%)	Amylose (%)	Lipid (%)	Protein (%)	Reference
A. Retroflexus	1			0.14	0.45	Goering, 1967
A. hypochondriacus	2		0, 14			Sugimoto, 1981
A. cruentus	4		0.1ī 11.1			Stone and Lorenz, 1984
A. hypochondriacus	2		0.2			Stone and Lorenz, 1984
A. hybridus	1		0.1			Stone and Lorenz, 1984
A. hybridus x *A. hypochondriacus*	1		0.3			Stone and Lorenz, 1984
A. hypochondriacus	1		4.9	0.39		Yanez et al., 1986
A. hypochondriacus	1		2.1	1.8	0.97	Paredes-López et al., 1989
A. paniculatus	1	61.2	11.5	1	0.98	Wankhede et al., 1989
A. hypochondriacus	1		2	0.62	0.1	Paredes-López and Hernández-López, 1991
A.cruentus	1			0.39	0.97	Gorinstein and Lii, 1992
A.cruentus	1		10.1	0.12	0.13	Perez et al., 1993b
A. hypochondriacus	1		10.6	0.00	0.13	Perez et al., 1993b
A. cruentus	1a		10.1	0ī 1.56	0.13ī 0.83	Perez et al., 1993a
A. hypochondriacus	1a		10.5ī 10.7	0.00ī 1.26	0.13ī 3.36	Perez et al., 1993a
A. cruentus	1	59		0.22	0.85	Babor et al., 1994
n.a.	1	50.3		0.06	0.34	Zhao and Whistler, 1994
A. hypochondriacus x *A. hybridus*	1b	50.6ī 58.7	5.79		0.02ī 0.06	Uriyapongson and Rayasduarte, 1994
A. cruentus	1b	50.4ī 65.1	6.81		0.02ī 0.05	Uriyapongson and Rayasduarte, 1994
A.cruentus	1			0.01	0.02	Mundigler, 1998
A. cruentus	1c	43.2ī 50.3	2.1		0.08ī 0.4	Radosavljevic et al., 1998
A. hypochondriacus x *A. hybridus*	1		0	1.02		Baker and Rayas-Duarte, 1998a
A. hypochondriacus	1	65.2		0.2	0.9	Bello-Pérez et al., 1998
A. cruentus	3	29ī 38.3	3.5ī 4.8	0.21ī 0.35		Hoover, 1998
A. cruentus	1		7.8			Qian and Kuhn, 1999
A. cruentus	14d	22 ± 18.5	19.2 ± 14.2			Wu and Corke, 1999
A. cruentus	34e	19.5 ± 15.1	25 ± 15.7			Wu and Corke, 1999
A. hybridus	8d	7.9 ± 2.2	19.8 ± 4.8			Wu and Corke, 1999
A. hybridus	6e	5.3 ± 2.1	22.3 ± 6.6			Wu and Corke, 1999
A. hypochondriacus	6	37.6 ± 16.6	7.8 ± 12.7			Wu and Corke, 1999
A. pumilus	3	5.1 ± 0.4	19.7 ± 6.9			Wu and Corke, 1999

A. retroflexus	3	6.1 ± 0.6	34.3 ± 3.5			Wu and Corke, 1999
A. spinosus	4	3.2 ± 1.3	18.1 ± 11.6			Wu and Corke, 1999
A. tricolor	8	4.0 ± 1.0	29.0 ± 9.9			Wu and Corke, 1999
A. viridis	3	2.0 ± 0.3	12.9 ± 8.0			Wu and Corke, 1999
A. cruentus	1			0	0.43	Calzetta Resio et al., 2000
A. hypochondriacus	1		4.2	0.87	0.05	Marcone, 2001
A. pumilus	1		8.2	1.1	0.07	Marcone, 2001
A. cruentus	1	52.1	3.2	0.1	0.1	Choi et al., 2004
A. cruentus	11		4.7ī 12.5			Kong et al., 2009
A. paniculatus	1		8.9			Kong et al., 2009
A. hypochondriacus	2		5.4ī 5.8			Kong et al., 2009
A. hybridus	1		6.1			Kong et al., 2009
A. cruentus	1		0.82	0.02	0.013	Tapia-Blacido et al., 2010
A. caudatus	1		13.6	0.019	0.09	Tapia-Blacido et al., 2010

No., number of genotypes tested in the specific study; a, three methods; b, three methods; c, five varying conditions based on one method; d, grown in Beijing, China; e, grown in Wuhan, China.

Table 2 Shape and size of granules

Species	Granule shape	Diameter (ε m)	Reference
A. hypochondriacus		0.75ī 1.25	Rao and Goering, 1970
A. hypochondriacus and *A. caudatus*	Round, polygonal	1	Tomita, 1981
A. cruentus and *A. hypochondriacus*	Angular, polygonal		Stone and Lorenz, 1984
A. hypochondriacus	polygonal	1	Paredes-López et al., 1989
A. paniculatus	eliptical	1.5ī 2	Wankhede et al., 1989
A. cruentus and *A. hypochondriacus*	angular and polyhedral	1	Perez et al., 1993b
A. cruentus	polygonal	0.5ī 1.4	Babor et al., 1994
A. cruentus	polygonal	0.5ī 1.5	Radosavljevic et al., 1998
A. cruentus	polygonal	0.75ę1.5	Hoover et al., 1998
A. cruentus	polygonal	1ī 2	Qian and Kuhn, 1999
A. hypochondriacus	polygonal	~1.1	Marcone, 2001
A. pumilus	polygonal	~1.1	Marcone, 2001
A. cruentus	polygonal	1.15ī 1.31	Kong et al., 2009
A. paniculatus	polygonal	1.16	Kong et al., 2009
A. hypochondriacus	polygonal	1.09ī 1.05	Kong et al., 2009
A. hybridus	polygonal	1.21	Kong et al., 2009

Table 3 Crystalline pattern and crystallinity

Species	No.	X-ray pattern	Crystallinity (%)	Reference
A. cruentus	1	A		Gorinstein and Lii, 1992
A. cruentus	3	A		Hoover et al., 1998
A. cruentus	1	A	45.5	Qian and Kuhn, 1999
A. cruentus	6	A	24.5ī 27.7	Kong et al., 2010
A. hypochondriacus	1	A	27.9	Kong et al., 2010

No., number of genotypes tested in the specific study.

Table 4 Molecular structure of amylopectin

Species	No.	fa (wt%)	fb1 (wt%)	fb2 (wt%)	fb3 (wt%)	CL	A (mole%)	ű,ɓ-Limit (%)	ECL	ICL
A. cruentus	10	20.6ī 23.5	42.9ī 45.6	12.1ī 12.6	21.3ī 23.1	17.4ī 18.2	51.8ī 54.5	54.8ī 56.8	11.1ī 11.9	5.2ī 5.6
A. paniculatus	1	22.1	43.4	12.6	20.8	17.8	52.7	55.5	11.4	5.4
A. hypochondriacus	2	23.8ī 24.1	42.6ī 43.1	11.5ī 12.0	21.6ī 22	17.4	52.1ī 52.3	53.9ī 55.5	10.9ī 11.2	5.3ī 5.5

Data from Kong et al., 2008; No., number of genotypes tested in the specific study; fa, (DP 6ï 12); fb1 (DP 13ï 24); fb2 (DP 25ï 36); fb3 (DP Ó37); CL, chain length; A (mole%), molar amount of A-chains in amylopectin; ű,ɓ-Limit (%), ű,ɓ-limit value (%); ECL, external chain length of amylopectin; internal chain length of amylopectin.

Table 5 Molecular structure of clusters in amylopectin

Species	No.	DP	NC	IC-CL	a (mole%)	IB-CL	NBbl
A. cruentus	2	57	8.8ī 9.1	13.8	49.2ī 50.1	6.8	6.0ī 6.1

Data from Kong et al., 2009b; No., number of genotypes tested in the specific study; DP, degree of polymerization; NC, number of chain per cluster; IC-CL, inter-cluster chain length; a (mole%), molar amount of a-chains for cluster; IB-CL, inter-block chain length; NBbl, number of building blocks per cluster.

Table 6 Gelatinization parameters measured by differential scanning calorimetry

Species	Starch:water and scanning rate	No.	T_o (°C)	T_p (°C)	T_c (°C)	ΔH	Reference
A. hypochondriacus	1:2, 5 °C/min	2	59–63	67–70	76–78	1–2.5 cal/g	Tomita, 1981
A. caudatus	1:2, 5 °C/min	3	51–53	56–57	63–65	1.2–1.6 cal/g	Tomita, 1981
A. hypochondriacus	1:2, 5 °C/min	3	66–68	72–75	77–82	2.4–3.4 cal/g	Konishi, 1985
A. caudatus	1:2, 5 °C/min	3	51–53	56–57	63–65	1.2–1.6 cal/g	Konishi, 1985
A. hypochondriacus	1:3, 10 °C/min	1		71.5		5.9 cal/g	Paredes-López et al., 1989
A. hypochondriacus	1:5.6, 10 °C/min	1	61.3	64.8	73.7		Paredes-López and Hernádez-López, 1991
A. cruentus	n.a., 10 °C/min	1	58.8	66.3	79.4	3.1 cal/g	Gorinstein and Lii, 1992
A. hypochondriacus x *A. hybridus*	1:2, 5 °C/min	1	63.3	67.8	75.9	20.2 J/g	Uriyapongson and Rayasduarte, 1994
A. cruentus	1:2, 5 °C/min	1	69.1	72	79.3	11.7 J/g	Uriyapongson and Rayasduarte, 1994
A. cruentus	1:3.25, 10 °C/min	2	64.7–64.5	76.6–78.1	84.9–85.7	7.1–9.1 J/g	Wu et al., 1995
A. cruentus	1:3, 10 °C/min	1a	65.5–70.6	69.2–74.3	77.7–82.9	14.4–15.0 J/g	Radosavljevic et al., 1998
A. hypochondriacus x *A. hybridus*	1:2.3, 10 °C/min	1	66.2	70.6			Baker and Rayas-Duarte, 1998a
A. cruentus	1:3, 10 °C/min	3	68.7–69.8	75.8–78.5	83.6–87	12.3–14.5 J/g	Hoover, 1998
A. cruentus	1:3.75, 10 °C/min	1	66.3	74.5	86.9		Qian and Kuhn, 1999
A. cruentus	1:3,	14b	68.8 ± 2.5	77.8 ± 1.8	89.1 ± 1.3	13.1 ± 2.7	Wu and Corke,

	10 °C/min					J/g	1999
A. cruentus	1:3, 10 °C/min	34c	62.3 ± 2.0	78.0 ± 1.7	89.6 ± 1.8	13.3 ± 1.8 J/g	Wu and Corke, 1999
A. hybridus	1:3, 10 °C/min	8b	66.8 ± 2.8	75.3 ± 3.2	86.8 ± 3.0	8.7 ± 1.5 J/g	Wu and Corke, 1999
A. hybridus	1:3, 10 °C/min	6c	68.0 ± 2.7	78.8 ± 2.6	89.1 ± 1.3	10.8 ± 2.3 J/g	Wu and Corke, 1999
A. dubius	1:3, 10 °C/min	3	72.4 ± 1.1	82.0 ± 1.0	91.4 ± 1.2	8.4 ± 1.7 J/g	Wu and Corke, 1999
A. hypochondriacus	1:3, 10 °C/min	6	66.1 ± 2.0	73.9 ± 2.0	88.8 ± 1.0	14.5 ± 1.0 J/g	Wu and Corke, 1999
A. pumilus	1:3, 10 °C/min	3	69.6 ± 0.7	76.1 ± 0.5	86.5 ± 1.5	7.3 ± 0.8 J/g	Wu and Corke, 1999
A. retroflexus	1:3, 10 °C/min	3	68.9 ± 2.0	78.1 ± 1.4	89.2 ± 1.1	11.2 ± 0.6 J/g	Wu and Corke, 1999
A. spinosus	1:3, 10 °C/min	4	67.6 ± 1.3	79.6 ± 0.7	90.6 ± 2.6	8.6 ± 3.3 J/g	Wu and Corke, 1999
A. tricolor	1:3, 10 °C/min	8	73.0 ± 2.5	82.0 ± 1.3	91.5 ± 1.2	10.0 ± 2.3 J/g	Wu and Corke, 1999
A. viridis	1:3, 10 °C/min	3	71.9 ± 0.7	80.2 ± 0.9	87.9 ± 3.3	6.7 ± 1.4 J/g	Wu and Corke, 1999
A. cruentus	1:3, 10 °C/min	1	65.4	73.3	85.0	10.0 J/g	Calzetta Resio and Suarez, 2001
A. hypochondriacus	1:3.3, 5 °C/min	1	62	70.6	78.9	13 J/g	Marcone, 2001
A. pumilus		1	63.4	71.6	80	12.2 J/g	Marcone, 2001
A. cruentus	1:3, 10 °C/min	1	69.3	74.9	83.2	10.6 J/g	Choi et al., 2004
A. cruentus	1:3, 10 °C/min	11	64.6ī 72.5	70.5ī 77.8	79.3ī 83.7	15ī 18.4 J/g	Kong et al., 2009
A. paniculatus	1:3, 10 °C/min	1	69	74.8	81.7	16.7 J/g	Kong et al., 2009
A. hypochondriacus	1:3, 10 °C/min	2	63.4ī 66	68.8ī 71.4	78.8ī 79.8	15.8 J/g	Kong et al., 2009
A. hybridus	1:3, 10 °C/min	1	68.1	73.4	81.2	16.7 J/g	Kong et al., 2009
A. cruentus	10 °C/min	1	69.5	73.4	89.5	14.4 J/g	Tapia-Blacido et al., 2010
A. caudatus	10 °C/min	1	69.5	73.4	89	13.5 J/g	Tapia-Blacido et al., 2010

No., number of genotypes tested in the specific study; a, two methods of isolation used; b, grown in Beijing, China; c, grown in Wuhan, China.

Table 7 Swelling power and solubility of granules

Species	No.	Parameter	Temperature (°C)					Reference
			50	60	70	80a	90b	
A. paniculatus	1	SP	10.3	12.9	15.1	30.2	35.1	Wankhede et al., 1989
		S	15.5	25.5	45.4	47.8	55.5	Wankhede et al., 1989
A. cruentus	1	SP	3.46			15 (85)		Perez et al., 1993b
		S	3.89			93 (85)	100(95)	Perez et al., 1993b
A. hypochondriacus	1	SP	3.28			17.5 (85)		Perez et al., 1993b
		S	4.54			92 (85)	100(95)	Perez et al., 1993b
A. cruentus	1	SP	3.7	7.1	22.1	26.9		Babor et al., 1994
		S	3.2	5.6	85.7	91.3		Babor et al., 1994
A. hypochondriacus	1	SP		10.8			20	Bello-Pérez et al.1998
A. cruentus	3	SF				40ī 55		Hoover, 1998
A. cruentus	1	SP	2.27		8.85	9.19	9.82	Calzetta Resio et al., 2000
	1	S	1.48		1.85	21.2	33.3	Kong et al., 2009
A. cruentus	11	SP				9.1ī 20 (85)		Kong et al., 2009
		WSI				16.1ī 95.3 (85)		Kong et al., 2009
A. paniculatus	1	SP				10 (85)		Kong et al., 2009
		WSI				78		Kong et al., 2009
A. hypochondriacus	2	SP				12.3ī 13.1 (85)		Kong et al., 2009
		WSI				90ī 91 (85)		Kong et al., 2009
A. hybridus	1	SP				10.5 (85)		Kong et al., 2009
		WSI				85.1 (85)		Kong et al., 2009

SP, swelling power (g/g/); S, solubility (%); WSI, water soluble index (%); No., number of genotypes tested in the specific study; a, figure in parenthesis indicates the actual temperature used was 85 °C; b, figure in parenthesis indicates the actual temperature used was 95 °C.

Table 8 Pasting characteristics

Species	Method	Starch content (w/v, %)	No.	Pasting temperature (°C)	Peak viscosity	Breakdown	Setback	Reference
A. paniculatus	BVA	10	1	67	455			Wankhede et al., 1989
A. hypochondriacus	BVA	10	1	67	400			Yanez et al., 1986
A. paniculatas	BVA	5	1		230			Sudhakar et al., 1992
A. hypochondriacus	RVA	10.4	1a	73ī 78	21ī 28	9ī 15	7ī 10	Perez et al., 1993b
A. cruentus	RVA	10.4	1a	70ī 72	26ī 36	10ī 21	8ī 15	Perez et al., 1993b
A. hypochondriacus	RVA	10.4	1b	73ī 74	18ī 22	15ī 18	0ī 7	Perez et al., 1993a
A. cruentus	RVA	10.4	1b	70ī 74	23ī 47	11ī 29	7ī 19	Perez et al., 1993a
A. hypochondriacus	RVA	7.14	1		17		15	Bahnassey et al., 1994
A. hypochondriacus x *A. hybridus*	BVA	6	1c	66.7ī 67.5	253ī 428		247ī 415	Uriyapongson and Rayasduarte, 1994
A. cruentus	BVA	6	1c	68.3ī 71.5	302ī 425		313ī 415	Uriyapongson and Rayasduarte, 1994
A. cruentus	RVA	10	2		96ī 141	66ī 131	92ī 191	Wu et al., 1995
A. cruentus	BVA	8	3d	69.8ī 72	390ī 540		70ī 110	Hoover, 1998
A. cruentus	RVA	10.7	1	71.7	138.5	72.5	42	Qian and Kuhn, 1999
A. cruentus	RVA	10.7	14e		248 ± 83	75	38	Wu and Corke, 1999
A. cruentus	RVA	10.7	34f		288 ±	86	106	Wu and

					109			Corke, 1999
A. hybridus	RVA	10.7	8e		210 ± 78	27	40	Wu and Corke, 1999
A. hybridus	RVA	10.7	6f		213 ± 70	39	117	Wu and Corke, 1999
A. hypochondriacus	RVA	10.7	6		172 ± 56	45	49	Wu and Corke, 1999
A. pumilus	RVA	10.7	3		104 ± 20	2	121	Wu and Corke, 1999
A. retroflexus	RVA	10.7	3		222 ± 9	-1	65	Wu and Corke, 1999
A. spinosus	RVA	10.7	4		207 ± 82	-10	37	Wu and Corke, 1999
A. tricolor	RVA	10.7	8		162 ± 104	-14	14	Wu and Corke, 1999
A. viridis	RVA	10.7	3		172 ± 0	76	-6	Wu and Corke, 1999
A. cruentus	RVA	10.7	1	75.7	68.2	16.6	7.5	Choi et al., 2004
A. cruentus	RVA	10.7	11		103ī 275	31ī 86	23ī 82.2	Kong et al., 2009
A. paniculatus	RVA	10.7	1		205	76	42.3	Kong et al., 2009
A. hypochondriacus	RVA	10.7	2		167ī 200	74ī 85	23.5ī 27.4	Kong et al., 2009
A. hybridus	RVA	10.7	1		133	58	30.7	Kong et al., 2009

No., number of genotypes tested in the specific study; BVA, Brabender Viscoamylograph; RVA, Rapid Visco-Analyzer; the viscosity unit for BVA is BU and for RVA is RVU; a, pH 4,7, and 9 were used; b, 3 methods used; c, 3 methods used; d, pH 5.5; e, grown in Beijing; f, grown in Wuhan.

Table 9 Gel texture properties [a]

Species	No.	Hardness (g)	Adhesiveness (gÂ)	Reference
A. cruentus	14b	118 ± 97	-1.2 ± 1.8	Wu and Corke, 1999
A. cruentus	34c	172 ± 135	-1.5 ± 2.0	Wu and Corke, 1999
A. hybridus	8b	139 ± 64	-11.8 ± 10.5	Wu and Corke, 1999
A. hybridus	6c	129 ± 65	-9.8 ± 13.4	Wu and Corke, 1999
A. dubius	3	136 ± 97	-3.0 ± 5.2	Wu and Corke, 1999
A. hypochondriacus	6	55 ± 95	-7.8 ± 10.9	Wu and Corke, 1999
A. pumilus	3	114 ± 112	-1.7 ± 2.9	Wu and Corke, 1999
A. retroflexus	3	289 ± 36	-3.3 ± 0.6	Wu and Corke, 1999
A. spinosus	4	240 ± 55	-7.5 ± 10.6	Wu and Corke, 1999
A. tricolor	8	194 ± 86	-7.8 ± 8.8	Wu and Corke, 1999
A. viridis	3	70 ± 11	-63 ± 13	Wu and Corke, 1999
A. cruentus	11	32ī 170	-88ī 846	Kong et al., 2009
A. paniculatus	1	69	-574	Kong et al., 2009
A. hypochondriacus	2	34ī 50	-130ī 131	Kong et al., 2009
A. hybridus	1	18	-26	Kong et al., 2009

No., number of genotypes tested in the specific study; a, gel with water content of 10.7% were put at 4 ^{o}C for 24 h before texture profile analysis (TPA); b, grown in Beijing; c, grown in Wuhan.

Table 10 Retrogradation measured by DSC

Species	Storage time (d)/ temperature (^{o}C)	Starch:water	No.	T_o (^{o}C)	T_p (^{o}C)	T_c (^{o}C)	ΔH (J/g)	R (%)	Reference
A. cruentus	28/4	1:3	1a	45.2–45.9	52.8–54	60–62.5	5.1–6.6		Radosavljevic et al., 1998
A. hybridus x *A. hypochondriacus*	21/25	1:2.3	1	48.8	59.3			24.7	Baker and Rayas-Duarte, 1998b
A. hybridus x *A. hypochondriacus*	21/4	1:2.3	1	37.7	48.9			55.3	Baker and Rayas-Duarte, 1998b
A. hybridus x *A. hypochondriacus*	21/–20	1:2.3	1	41.9	49.1			32.8	Baker and Rayas-Duarte, 1998b

No., number of genotypes tested in the specific study; R%, degree of retrogradation; a, two methods used.

Table 11 *In vitro* Ŭ-amylolysis of granular and gelatinized starches

Species	Form	No.	Enzyme type	Time	Hydrolysis (%)	Reference
A. paniculatus	Granular	1	Glucoamylase	100 min	25.5	Wankhede et al., 1989
A. paniculatus	Granular	1	Human salivary Ŭ-amylase	100 min	18.5	Wankhede et al., 1989
A. cruentus	Granular	3	Porcine pancreatic Ŭ-amylase	30 min	8.7ī 59.6	Hoover, 1998
A. cruentus	Granular	3	Porcine pancreatic Ŭ-amylase	60 min	62.5ī 76.2	Hoover, 1998
A. cruentus	Granular	3	Porcine pancreatic Ŭ-amylase	180 min	74.3ī 80.1	Hoover, 1998
A. paniculatus	Gelatinized	1	Glucoamylase	100 min	87.7	Wankhede et al., 1989
A. paniculatus	Gelatinized	1	Human salivary Ŭ-amylase	100 min	67.5	Wankhede et al., 1989
A. hypochondriacus	Gelatinized	1	Porcine pancreatic Ŭ-amylase	60 min	63.5	Yanez et al., 1986

No., number of genotypes tested in the specific study.

Table 12 Chemical and physical modifications

Species	Chemical modification								Physical modification			
	CL	AC	OXID	Substitution HP	SY	OS	CM	PHO	HMT	ANN	ɔI	HSP
A. cruentus	1, 2	3		6, 7				15	2			18
A. hypochondriacus	1	3								16	17	
A. paniculatas			4, 5	8	9, 10	11, 12	13, 14				17	

CL, Cross linking; AC, acid treatment; CM, carboxymethylation; OXID, Oxidization; HP, Hydroxypropylation; SY, Succinylation; OS, octenyl succinylation; HMT, heat-moisture treatment; ANN, annealing; ɔI, ɔ-irradiation; HSP, High-hydrostatic pressure; 1, Perez et al., 1993b; 2, Gunaratne and Corke, 2007; 3, Kong et al., 2012; 4, 5, Chattopadhyay et al.,1997 and 1998; 6, 7, Pal et al., 2000, 2002; 8, Kshirsagar and Singhal, 2008; 9, 10; Bhandari and Singhal, 2002a and b; 11, 12, Bhosale and Singhal, 2006, 2007; 13,14, Bhattacharyya et al., 1995a and b; 15, Hanson, 1998; 16, Paredes-López and Hernádez-López, 1991; 17, Kong et al., 2009c; 18, Linsberger-Martin et al., 2012.

Table 13 Application of amaranth starches for food and non-food purposes

Species	Treatment	Application	Characteristics	Reference
A. paniculatas	Native form	As biodegradable fillers in the formation of low density polyethylene films	Inexpensive; Amaranth starch achieved minimum decrease in the tensile strength of film compared with corn starch with larger granules	Ahamed et al., 1996
A. paniculatas	Native form	As thickener in the printing of Indigosol and Vat dyes on cotton in textile industry	Available at a cheaper rate locally; Better flow properties than maize starch; Could replace maize/wheat starches	Teli et al., 1996, Teli et al., 2007 and 2009
A. paniculate	Native form	As substrate for the synthesis of super-absorbents grafted with acrylamide and acrylic acid	Maximum absorbency of water 155 g/g	Teli and Waghmare, 2010
A. caudatus & A. hypochondriacus	Native form	Formation of plastic sheets with synthetic thermoplastics		Wilhelm et al., 1998
A. cruentus	Native form	As substrate for cyclodextrins production	Ŭ-, ɓ-, and ɔ-Cyclodextrins produced simultaneously by glycosyltransferase	Urban et al., 2012
A. paniculatus	Native form	Composite flour of soya flour and starch in deep-fat fried noodle like snacks	Amaranth starch incorporation reduced the oil content in the fried snacks	Ahamed et al., 1997
-	Native form	As fat replacer in	Up to 50% of the fat in a frozen dessert	Malinski et al.,

		frozen desserts	may be replaced by starch	2003
A. cruentus	Phosphorylation	As fat replacer in mayonnaise	Sensory attributes (creaminess, oily cling, and graininess) remain the same after replacement	Hanson, 1998
A. paniculatus	Hydroxypropylation	Hydroxypropylated starch used for microencapsulation of flavors	Excellent agent for encapsulating lemon oil	Kshirsagar and Singhal, 2008
A. paniculatus	Oxidization	Oxidized starch as substitute of gum arabic in flavor encapsulation	Little hygroscopicity and similar encapsulation efficiency	Chattopadhyay et al., 1998

Figure captions:

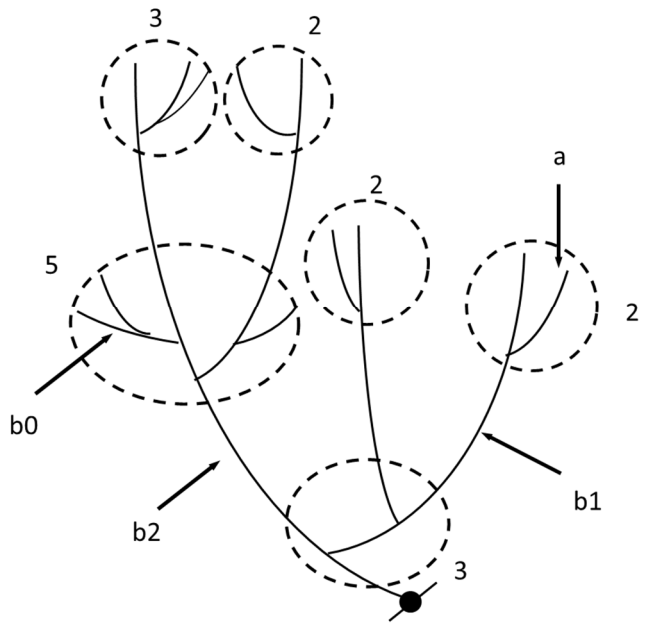

Figure 1. A possible model of an amaranth amylopectin cluster in the form of ű,ɓ-limit dextrin based on data from Kong et al. (2009) and adapted from (Pérez and Bertoft, 2010). Building blocks are encircled by dashed line and numbered (2, 3, or 5) according to their number of chains. Different categories of chains (b0, b1, and b2) in the cluster are indicated with arrows.