PROPERTIES OF PEARL MILLET: NATIVE AND MODIFIED STARCH

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Abstract

Pearl millet (Pennisetum typhoideum) is termed as an “orphan crop” or even “lost crop” despite the fact that it staples for millions of people in the semi-arid regions of the world particularly Africa and India. It is recognized as being the most widely grown of all the millet type. Pearl millet is mostly used as whole flour for traditional food preparation and hence confined to traditional consumers and to people of lower economic strata. Though it improves nutritional quality, due to the presence of antinutritional factors, its utilization is limited. The major component of millets is starch, which may amount up to 70 % of the seed and determines the quality of millet products. This review summarizes the current knowledge of the isolation, chemical composition, structure, physicochemical properties, modifications, and uses of millet starch. The isolated starch from pearl millet may be used as a low cost and nutritional ingredient in infant foods and functional food products such as beverages, custard and soup mixes etc. Due to its gluten-free nature, pearl millet can be successfully used in bread, cookies or breakfast items.

Keywords: Pearl millet, Isolation of starch, Gluten free, Physical properties, Modification.
INTRODUCTION

The term “millet” is broadly used to describe various small seeded grasses that are harvested for food or feed. They can be classified within the genera *Brachiaria, Digitaria, Echinochloa, Eleusine, Panicum, Paspalum, Pennisetum, Setaria* and *Sorghum* (Adeola et al. 1995). Several species of millets exist, including pearl (*Pennisetum glaucum*), brown top (*Brachiaria ramosa*), barnyard (*Echinochloa crus-galli*), finger (*Eleusine coracana*), proso (*Panicum miliaceum*), kodo (*Paspalum scrobiculatum*), little (*Panicum sumatrense*), and foxtail (*Setaria italica*). Amongst these millet species, pearl millet is the most widely cultivated crop.

Millets are ancient crops and have been cultivated by man for thousands of years. Millets are mainly produced in Asian and African countries, with India being the largest producer (FAO 2012). Pearl millet (*Pennisetum typhoideum*), is also classified as *P. glaucum, P. americanum*, and is locally known as *bajra* in India (Taylor 2004). It ranks third after wheat (*Triticum aestivum*) and rice (*Oryza sativa*) (GOI, 2008). Millets have been reported to be nutritionally superior when compared to many bowls of cereal (Parameswaran and Sadasivam 1994; Saleh et al. 2013). They are good sources of proteins, carbohydrates, fiber and essential amino acids. Millets are also rich in phytochemicals and micronutrients (Singh et al. 2012). Health benefits associated with the consumption of millets have been documented (Shobana et al. 2009). Nutritionally, pearl millet makes an important contribution to human diet due to high levels of calcium, iron, zinc, lipids and high-quality proteins. Pearl millet contains about 9 to 13% protein, 8% fat, which is higher than rice, barley, maize, and sorghum (Desikachar 1975; Lai et al. 1980). The ash content of pearl millet ranges from 1.6 to 3.6% (Serna et al. 1995). Besides, it is also a rich source of dietary fiber and micronutrients. Starch is the major constituent of pearl millet (AnuSehgalet al. 2006; Malik et al. 2002).
Starch is an important biopolymer which is extensively used in many food products. It enhances the textural properties of food and it is commonly used as a thickener, colloidal stabilizer, gelling agent, bulking agent and water retaining the agent in food and pharmaceutical products (Singh et al. 2007). Regardless of its key functional roles, native starch affects several quality characteristics of food products and renders instability of paste under shear, acid or freezing conditions, and poor paste clarity. So, in order to overcome these undesirable changes, native starches are usually modified either chemically or physically or using a combination of both. Modifications bring about the desirable alteration in the structure of starch which subsequently improves its functionality in food products (Tharanathan 2005).

STRUCTURE OF PEARL MILLET

Taylor et al. (2010) reported that the millet grain is about one-third the size of wheat, however, despite its small grain size; pearl millet has relatively good nutritional value compared to other cereal grains. This is because of its proportionally large germ compared to the endosperm. Pearl millet grains are shaped like a liquid drop. They can be up to 2 mm in length and their weight ranges between 3 mg and 15 mg. This is a small grain in comparison with other tropical cereal grains such as maize and sorghum (Jain and Bal 1997). Serna-Saldívar and Rooney (1995) stated that the pearl millet grain comprises about 8% pericarp, 17% germ (which is proportionally large) and 75% endosperm. Similar to values of 7.2 to 10.6%, 15.5 to 21% and 71 to 76%, for pericarp, the germ (embryo) and the endosperm was reported by Abdelrahman and Hoseney (1984). In contrast, Zeleznak and Varriano-Marston (1982) estimated that the germ forms about a one-third of the kernel, and the endosperm between 50 to 60% of the kernel. The observed differences may be because of differences in the varieties of pearl millets studied.

The last major structural component of the pearl millet kernel is the germ (embryo). The pearl millet germ to endosperm ratio is higher than that of other cereals (Serna-Saldívar and Rooney 1995). The germ comprises two major parts: the scutellum cells and embryonic axis. The scutellum serves as a storage body for lipids, protein, enzymes and minerals (Serna-Saldívar and Rooney 1995) and acts as a transport system organ. Scutellum cells have a smooth round appearance and are between 25.0 to 35.0 μm in diameter (McDonough et al 1986).

NUTRITIONAL COMPOSITION OF MILLET

The average protein and fat contents of millet at 12% moisture are 11.8% and 4.8 % respectively (FAO 1995). These are comparable to values for maize (9.2% protein, 4.6% fat) and
sorghum (10.4% protein, 3.1% fat). Millet protein is a good source of essential amino acids except for lysine and threonine but is relatively high in methionine. Millets are also a rich source of phytochemicals and micronutrients (Mal et al. 2010). And they have been found to be significantly rich in resistant starch, dietary fibres (both soluble and insoluble), minerals, and antioxidants (Ragaee et al. 2006). Millets contain about dry matter (92.5%), ash (2.1%), crude fibre (2.8%), crude fat (7.8%), crude protein (13.6%), and starch (63.2%) (Ali et al. 2003).

Investigations by Abdalla et al. (1998) on 10 genotypes of pearl millet, showed that pearl millet contained 88-91% dry matter, 1.6-2.4% ash, 2.6-4.0% crude fibre, 2.7-7.1% oil, 8.5-15.1% crude protein, 58-70% starch and 354-796 mg\textsuperscript{-1} phytic acid. Mineral contents were 10-80, 180-270 and 450-990 mg\textsuperscript{-1} Ca, Mg and P, respectively and 70-110, 4-13, 53-70, 18-23, 10-18 and 70-180 mg\textsuperscript{-1} K, Na, Zn, Mn, Cu, and Fe, respectively. The nutrient composition of pearl millet in comparison to other cereal grains shows relatively high gross energy content of approximately 363 Kcal/100 g. This high energy content is due to the high-fat content of the grain, which is related to the large germ size. Pearl millet has the higher arginine, threonine, valine, isoleucine and lysine values than maize.

The major nutritional component of cereal grains, including pearl millet starch. Starch content of pearl millet varies from 50 to 75% of the grain composition (Hoover et al. 1996b; Oshodi et al. 1999; Hadimani et al. 2001; Shahidi and Naczk 2003) and is similar to the starch composition of sorghum. Aside from starch, the carbohydrates in pearl millet grain include free sugars and nonstarch polysaccharides (Hadimani et al. 2001). Pearl millet starch has lower amylose content than sorghum (Serna-Saldívar and Rooney 1995). The amylose content in pearl millet grain ranges between 17.0 to 21.5% (Taylor et al. 2004). Hadimani et al. (2001) and Hoover et al. (1996a) showed that the amylose content may be as high as 28.8 to 38% in some varieties, an indication of great variability in amylose content in pearl millet starch.

**STARCH AND ITS PROPERTIES**

Starch is one of the basic storage polymers in many plants. It consists of two types of molecules, branched amylopectin and linear amylose. Amylose is linear with a few branches (α-[1 → 6] linkage) scattered along the linear backbone (α-[1 → 4] linkage), whereas amylopectin has much more branches. In both cases, the building block is an a-D-glucopyranose residue, forming α-1,4-glucosidic bonds in linear structure of amylose and additional α-1,6-glycosydic branches in amylopectin molecules. The differences in the structure of both polymers result in
significant variance in their properties. Amylose is much more prone to the crystallization process, called retrogradation and can form tough gels and strong films, while amylopectin could be dispersed in water and retrogrades much slower, which results in soft gels and weak films (Fredriksson et al. 1998; Hoover 2001; Perez and Bertoft 2010). Native starch is organized in granules present in seeds, roots, and tubers, as well as in stems, leaves, fruits and even pollen. They differ in size and shape (spheres, ellipsoids, polygon, platelets and irregular tubules) depending mostly on botanical origin. A starch granule is partly crystalline, which significantly affects its properties (Singh et al. 2003). Though application of native starches is limited mostly to food aspects, the granules and polymers could easily be modified by chemical, physical and enzymatic means, which allows obtaining products with desirable physicochemical and functional properties (Pietrzyk et al. 2013; Tharanathan 2005). The chains and chain segments of both amylose and amylopectin can form the helical complex with iodine molecules in solution, giving rise to distinctive red and blue colors. The branches impart steric hindrance and the endogenous lipids in starch can compete with iodine molecules for helix formation (Delcour 2010). Gaffa et al. (2004) reported that the blue values for amylose and amylopectin of pearl millet were 1.3–1.41 and 0.18, respectively. Degrees of polymerization (DP) in pearl millet by number for amylose 1060–1250 and amylopectin 9000–9100, respectively. The molecular weights of amylose in the range of 105–106 and amylopectin 107, respectively (Wankhede et al. 1979; Madhusudhan et al. 1996)

**MODIFIED STARCHES IN FOOD**

Starch is the most important carbohydrate in the human diet. Starch modification leads to a structural change of the starch, that is obtained through physical, enzymatic, chemical (or the combination of these) applications. Modification of starch changes its properties like pasting, gelling, water absorption, digestibility, absorption and many other properties according to the need. Some studies are emphasized on the use of different chemical treatments to alter the properties of starches (Singh et al. 2007). Starches are modified as they show enhanced performance in different applications. The modification can be performed to starches to increase their steadiness against different conditions like extreme heat, acidic condition, shear, time, cooling or freezing to change their texture, to reduce or enhance their viscosity, to lengthen or shorten gelatinization time, or to increase visco-stability (Singh 2007).

**PHYSICAL MODIFICATION**
Various hydrothermal treatments (heat-moisture, annealing, and quenching) on finger millet starch have been reported (Premavalli et al. 2003; Adebowale et al. 2005). Heat-moisture treatment (HMT) is usually conducted at about 100 to 130 °C with a limited amount of moisture (35%). Annealing (ANN) refers to heating starch with the water content of ~40–65% at the temperature below the onset of gelatinization (Hoover 2010). Quenching (QUE) refers to the rapid cooling of an over-heated starch slurry to a much lower temperature (e.g. −180 °C) (Premavalli et al. 2004). These hydrothermal treatments would lead to interactions and reassociations of amylose and amylopectin chains in the granules, while ANN and HMT can improve the structural defects of the crystalline part in the granules. HMT and ANN increased the gelatinization temperatures and ΔH of finger millet starch whereas QUE decreased the temperatures of gelatinization (Premavalli et al. 2004; Adebowale et al. 2005).

Adebowale (2005) indicated that Finger millet starches show that HMT modifies the pasting properties of the native starch from Type B, which is characteristic of normal cereal starches to Type C which is characteristic of cross-linked or legume starches, while the ANN starch retains its Type C configuration. Also, the X-ray diffractogram of starch has the characteristic ‘A’ pattern of the cereals starches, although the ANN and HMT starches retain this pattern with lower intensities. These results were corroborated by the DSC results, which show an increase in the gelatinization temperatures (onset [To], peak [Tp], and conclusion [Tc]) on ANN and HMT of the native starch. The SEM results show little effect of ANN and HMT on the shape or surface characteristics of the granule, while the damage to granule was 1%.

CHEMICAL MODIFICATION

Chemical modification of potato starch in a two-step process has been studied. At the first stage the starch modifiers, i.e. isocyanate derivatives are synthesized. At the second step, starch was modified with the synthesized hexamethylene diisocyanate derivatives, N-methylpyrrolidone slurry. Modified starch exhibited acceptable bulk hydrophobic properties (swellability in water in a range of 2.0 - 2.5 cm³/g) and melt flow features in hot press test (Katarzyna&Tadeusz 2007).

Acids break the glycosidic linkages of α-glucan chains, altering the properties and structure of native starch. The amorphous region in granules is much more susceptible to acid hydrolysis than the crystalline part (Hoover 2000). Starches from three millet genotypes were subjected to acid hydrolysis (HCl 2.2M) at 25 °C for 20 days. Hydrolysis extent up to 88.2% was...
noted (Hoover et al. 1996a). The difference in the hydrolysis degree among the genotypes reflects the difference in granules and the physical associations and interactions between amyllose and amylopectin. Acid treatment can be used to produce starch nanocrystals, which is gaining a research focus recently (Hoover 2000).

The hydroxyl groups of starch can be reactive and substituted by various functional groups such as hydroxypropyl group. Carbon-13 nuclear magnetic resonance (NMR) spectroscopy revealed that hydroxypropylation of finger millet starch mostly occurred on the carbon 6th position. Hydroxypropylation resulted in reduced turbidity, pasting temperature and setback value, syneresis, and retrogradation, and increased peak viscosity of pasting properties (Lawal 2009).

**ENZYME MODIFICATION**

Resistant starches (RS) were prepared using pullulanase enzyme from banana starch by debranching for several times, after autoclaving treatment. The different treatments produced seven different RS products; these RS were tested for its available starch, RS and in vitro hydrolysis rate. The control sample (without debranching) had the highest starch availability of 80.5% and the lowest RS of 9.1%. Debranched sample showed the available starch content of 72% and RS of 18%. As this banana starch is a good source for RS preparation this can be a different source of RS in developing countries for obtaining a nutraceutical ingredient in the development of functional foods (Rosalia et al 2004).

Another study focused on modifying potato starch with enzymes. Amylomaltases is used to modify potato starch, resulting in the disappearance of the amyllose fraction and the formation of an amylopectin with a broadened side-chain composition. The amylo maltasetreated potato starch showed a thermoreversible gelling property, making it comparable to gelatin. As gelatin is of animal origin, it is not accepted by several consumers. Therefore, this may be a good plant derived substitute for gelatin (Marc et al. 2005). The starch was treated enzymatically in the granular state with a mixture of fungal a-amylase and glucoamylase and then chemically modified to produce enzyme hydrolyzedhydroxypropyl starch. This starch exhibits significantly different functional property compared to hydroxypropyl starch prepared from native starch. It is evident that the dual modification of starch using this technique provides a range of functional properties that can be adapted for specific applications (Karim et al. 2008).

**FUNCTIONAL PROPERTIES**
SWELLING AND SOLUBILITY CHARACTERISTICS

Wankhede et al. (1990) reported that increase in swelling factor and amylose leaching with increasing temperature for the millet starches, which was most predominant between 60 and 70 ºC was observed. The swelling factor of the pearl millet starches is higher than those of wheat and rice. Swelling and solubility behavior of starches in aqueous solutions are studied to investigate the nature of associated bonding forces within starch granules. Hoover et al. (1996) studied the swelling factor and amylose leaching of pearl millet starches at temperatures between 50-95 ºC. Abdallah et al. (1987) observed higher swelling factor for pearl millet compared to yellow corn and sorghum. Malleshi et al. (1986) observed a decrease in the swelling factor but an increase in the solubility of millet starches when germinated.

MariiumShaikh et al (2014) reported that Pearl millet starch hydrolyzed by 0.1 M HCl (PAT$_{0.1M}$) had higher swelling power compared to the control (PN) which is due to hydrolysis of long polymer chains into low molecular weight chains which thereby exposes more hydrophilic OH groups. Insertion of succinyl groups to PAT$_{0.1M}$ further increased the swelling power of starch from 13.1 g/g to 31.6 g/g. This drastic increment in swelling power is due to steric hindrance created by succinyl groups which in turn allowed higher percolation of water into the starch granules. The swelling power of PS was almost doubled compared to the control. Pearl millet starch acid thinned with 1 M HCl solution (PAT$_{1.0M}$), resulted in reduced swelling power which could be due to excessive hydrolysis of chains in the amorphous region of the starch that is more easily accessible to the reagents. Acid hydrolysis conducted with 1 M HCl solution showed higher solubility compared to one conducted with 0.1M HCl solution which is due to the presence of a greater number of linear and short polymer chains in PAT$_{1.0M}$ that leach out easily from the granule. The depolymerized chains cause internal weakening of the granule which subsequently increases the relative crystallinity, resulting in restricted swelling power of starch. However, an addition of succinyl groups on PAT$_{1.0M}$ significantly increased the swelling power of PAT$_{1.0M+S}$.

GELATINIZATION

When heated with sufficient amount of water over a range of temperature, granular starch undergoes an order–disorder phase transition termed gelatinization. Water uptake by the amorphous region, radial swelling of the granules, breakdown of the crystalline region with the disruption of double helices, and starch molecule leaching are the characteristics of gelatinization.
(Hoover 2001). Starch to water ratio at 1:2 and 1:3 gave a notable difference in the gelatinization parameters for the finger millet starch (Premavalli et al. 2005). Amylose-lipid complex melting quantified by DSC has been observed in starches from two pearl millet genotypes, and the ranges of To, Tp, Tc, and ΔH were 91.7–94.2 °C, 99.4–102.8 °C, 108–110 °C, and 1.1–1.5 J/g, respectively (Gaffa et al., 2004). Hoover et al. (1999) stated that the higher To, Tp, and Tc of ICMS 7703 (64.5-78°C) suggests that the crystallite size and/or crystallite association within its granules are of a higher order of magnitude than in ICPT 8203 (61.2-70.5 °C), ICMH 356 (60.9-67.5 °C) compared to wheat and corn starch.

PASTING PROPERTY

The pasting properties of starch are primarily changes that occur when starch is heated in excess water in the presence or absence of shear. These changes include swelling of starch granules, leaching of molecular materials from the granules and eventual disruption of the granules especially when shear is applied by Tester and Morrison (1990). Using the Brabenderviscoamylograph, significant differences are observed in the gelatinization temperature, peak viscosity, hot paste viscosity, cold paste viscosity, break down and set back. Beleia et al. (1980), in studying the pasting properties of pearl millets, reported a pasting temperature of 76.5 ºC. Differences between maximum and minimum viscosity at 95 ºC was 100 BU. Larger differences are observed between the pearl millet starches at 95 ºC for 1 hour and also during the cooling cycle. Hoover et al. (1996) also reported differences in the pasting properties of pearl millet varieties. They suggested viscosity differences observed at 95 ºC could be due to the degree of crystallinity, the extent of amylose leaching and amount of amylose lipids.

RETROGRADATION

When the gelatinized starch is subjected to cooling, the amylose and amyllopectin molecules interact with water and each other to recrystallize to form a more ordered structure. This process termed as retrogradation is influenced by various factors such as water content, storage condition and time, amylose content, the molecular structure of amyllopectin component, and the presence of non-starch components (e.g., lipid) (Hoover 2001). Retrogradation can be quantified by various methods with the ones used for millet starch being DSC and Rheometry (Hoover et al. 1996b; Ojijo and Shimoni 2007). Retrograded pearl millet starch had lower melting temperatures, broader melting temperature range, and lower ΔH compared with the
parameters of gelatinization (Hoover et al. 1996b), due to the much imperfect nature of the crystals formed as a result of retrogradation. A comparative DSC study showed that retrograded finger millet starch had lower to higher ΔH than that of foxtail, pearl, and prose millets (Annor et al. 2014).

Hoover et al. (1999) reported that $T_o$, $T_p$, and $T_c$, of the retrograded gels were lower than those for the gelatinization endotherm and $T_c$-$T_o$ for retrogradation was broader in three varieties of pearl millet than for gelatinization. The enthalpy of retrogradation (ΔHn) increased on storage in three varieties of pearl millet. The broadening of $T_c$-$T_o$ on retrogradation implies that the retrogradation endotherm probably reflects melting of crystallites of different stability, size or perfection formed by different types of starch chain associations (amylose-amylopectin and/or amylopectin-amylopectin) during gel storage. The increase in ΔHn on storage reflects the formation of double helices between A chains of amylopectin (Hoover et al. 1994).

**FREEZE–THAW STABILITY**

In some scenarios during food processing and preservation, starchy food needs to go through freeze–thaw cycles. The freeze–thaw stability of millet starch has been quantified by the amount of water separated from starch gel after freeze–thaw cycles (syneresis) (Yanez et al. 1991; Hoover et al. 1996). Pearl millet starch showed better stability than corn and wheat starches (Hoover et al. 1996). The freeze–thaw stability of starch is influenced by thermal history, molecular structure and contents of amylose and amylopectin, water content, and so on. The lower amount of amylase and abundance of shorter unit chains of amylopectin may be related to good freeze–thaw stability of native starch (Srichuwong et al. 2005).

**MORPHOLOGICAL GRANULAR CHARACTERISTICS OF THE STARCHES**

Hoover et al. (1990) reported starch granule sizes of 2-22 μm for three varieties of pearl millets. Wankhede et al. (1990) reported that granule size ranges of 10-16 μm were also have been reported for pearl millet. The differences observed in the shapes and sizes of the millet starch could be due to the fact that the individual starch granules are at different stages of maturity at the time the millet seeds are harvested and starches isolated. X-ray diffraction pattern of pearl millet starches showed the A-Type x-ray pattern and indicated that the HMP 550 Starch was more crystalline than the HMP 700 sample, which may explain the higher cold water inhibition by the latter starch.
The X-ray diffraction analysis of native starches yields two types of spectral patterns, A type and B type, which points to two types of crystalline structures. Cereal starches yield the A-type pattern, whereas the tuber starches and amylose-rich starches yield the B-type pattern. Englyst et al. (1992) stated that legume starches yield C type pattern which is the combination of the A and B patterns. In general, starch granule showing X-ray diffraction patterns of the B or C type tend to be more resistant to digestion by pancreatic amylase and the degree of resistance is dependent on the plant source. This type of resistance to hydrolysis with pancreatic amylase affects the digestibility of starchy foods normally eaten raw such as banana, and processed foods, such as biscuits, where the starch has been incompletely gelatinized. Though potato and cassava are both tubers, but cassava is more susceptible to α-amylase hydrolysis than potato, probably due to differences in their starch granules’ surface areas. Potato starch granules (B-type) are very large and therefore have a low surface area relative to volume compared with tapioca starch granules (B-typespherulites), which are rapidly fragmented by amylases, a process that increases the area exposed to attacking enzymes. The starches did not show any peak at $2\theta=5.6^\circ$ for B-type starch indicating the typical A pattern of the starches Singh et al. (2011). Starch obtained after each purification stages showed a single peak and a dual peak, respectively at $2\theta=23.2^\circ$ and $2\theta=17–18.1^\circ$, observed for starches from different maize types (Singh et al. 2006).

CONCLUSION

Starch and its derivatives, including modified starches, play an important role in gluten free products. In the absence of gluten, starch becomes the main texture and structure-forming component in many systems. Resistant Starch shows improved crispness and expansion in certain products and better mouth feel, color, and flavor over products produced with some traditional, insoluble fibers. It is ideal for use in Ready to eat cereals, snacks, pasta/ noodles, baked goods, and fried foods and permits for easy labeling as simply starch, conferring additional nutraceutical benefits. Resistant Starch has properties similar to fiber and shows promising physiological benefits in humans, which may result in disease prevention. Foods containing high levels of Resistant Starch yield fewer calories and lower glycemic loads important formulation considerations for diabetics as well as the weight-conscious. Apart from native starch, gluten-free products may contain starch modified by chemical, physical or enzymatic treatment. Pearl millet starch contains $50 – 75\%$ grain composition. The changes
involved in the modification of pearl millet starches are the mitigation of the inherent shortcoming in the native starches such as loss of viscosity, easily to retrograde, insolubility and loss of ordered structure that ultimately provides the feasibility basis for wide application of starches. The physical and dual modification with a large number of involved techniques. Heat-moisture treatment improved heat and shear stability, reduced retrogradation and increased resistant starch of pearl millet starch. Chemical modification increased the pasting temperature of some modified pearl millet starches, whereas peak viscosity, trough, setback and breakdown values all reduced after modifications in pearl millet starch. However, a tendency for retrogradation reduced after modification as shown in setback value. In addition to promoting utilization of millet grains in the urban area to open new materials for farmers to improve their income, developing highly improved products from millet is needed.

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