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Millets Starch and Its Functionality

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Introduction

Millets are small grain crops belonging to the *Poaceae* family. They are also called as *primitive grains* and were widely consumed as staples much before wheat and rice emerged and became the major staples. The rediscovery of these grains has shifted their status from *poor man's staple to nutricereals and have become the food for elite class*.

Millets are widely cultivated in India and are classified into major and minor millets on the basis of production and size of the grains. The major millets include sorghum (*jowar*), pearl (*bajra*) and finger millets (*ragi*) while foxtail (*kangni*), little (*kutki*), kodo, proso (*chena*), barnyard (*sanva*) millets are categorized as minor millets. Millets are rich in carbohydrates (65-75%) proteins (7-12%), fats (2-5%), dietary fibre (15-20%), micronutrients such as vitamins and minerals as well as phytochemicals. The amino acid profile of millets is better than the commonly consumed cereals. Hence the nutricereals are have balanced and adequate amounts of nutrients to meet out the recommended dietary intakes of people in different age groups.

The carbohydrates present in millets mainly comprise of glucose, sucrose, fructose, raffinose, stachyose and starch. Starch contributes to 55-65% of the total carbohydrates present (60-70%).Characterization of millet starch revealed that it is made up of amylopectin (80%) and amylose (20%). Amylopectin has a branched chain structure and is a polymer of D-glucose monomer units linked by α-1,4- and α-1,6-glycosidic linkages. It swells to form a viscous gel with water, however, the solubility is less in hot water. The presence of α-1-6 glycosidic bonds on the branched chains reduces its potential for hydrogen bonding. Amylose on the other hand is a straight chain structure comprising of D-glucose monomer units linked by α-1,4-glycosidic linkage. It is soluble in hot water forming helical structure that does not form inter-strand hydrogen bonds and expands easily. This allows easy penetration of water and enzymatic hydrolysis of α-1,4-glycosidic linkage resulting into glucose units by α-amylase.The morhphological characteristics, molecular weight, degree of crystallinity and

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physico-chemical properties of millet starch determines the functional properties, hence its use and wider applications can be explored in food processing sector.

The technological advancement in research and food processing calls for a variety of millet based products. The production and quality of these products largely depends on the composition, structures, properties, and interaction of starch. In its native form, starch does not possess functional properties, however, processing results in its modification to meet the desired physico-functional properties of various food products.

Millet starch

The starch content of millets varies between 55-65%. Millet starches generally comprises of 70-80% amylopectin and 20-30% amylose. Amylose is about one fourth of amylopectin concentration, however, the ratio of amylose to amylopectin largely depends on the source of starch. The shape and size of starch in different millets varies as depicted in Table 1. The inclusion of additional substances such as lipids, fiber, proteins and bioactive components act as impurities to starch granules and have a substantial impact on their functional properties. Millets mainly contains polar phospholipids (89%), and nonpolar lipids, called triglycerides (11%). Due to the cohesive and hydrophobic properties, lipids tend to form complexes with the amylose thereby affecting the swelling capacity and flowability of starch during processing. Millets are rich in fibers and they decrease the uptake of oil, thus they can impair oil binding ability during food formulations. Additionally, proteins contain both hydrophobic and hydrophilic components which determine their capacity to bind with both water and oil. The bioactive components also affect the physicochemical properties of millet starch. Notably addition of polyphenols to starch alters the viscosity of the food products.

Table 1Shape and size of various millet starches

Millet	Carbohydrate (g/100g)	Starch (g/100g)	Shape	Size (µm)
Sorghum millet	67.68	59.70	Polygonal, spherical and slightly round	2-12
Pearl millet	61.78	55.21	Polygonal with pores on surfaces	3-15
Finger millet	66.82	62.13	Polyhedral shape with a smooth surface	9.9-11.2

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Foxtail millet	60.09	-	Small spherical, small polygonal (especially pentagonal) large pentagonal	0.8-9.6
Kodo millet	66.19	64.96	Large polygonal, rarely small spherical and polygonal	1.2-9.5
Little millet	65.55	56.07	Small spherical; large spherical	1.0-9.0
Proso millet	70.04	-	Small spherical, large spherical (rare) large polygonal	1.3-8.0
Barnyard millet	65.55	-	Small spherical, large spherical large polygonal	1.2-10.0

Processing of millet starch

Starch may be processed using physical, chemical, enzymatic processes as shown in Figure 1. Endosperm part of every cereal grain contains starch and protein which are firmly linked to each other. Different techniques are available for solubilisation of the proteins and isolation of starch from grains. Selection of extraction technique depends upon the functional properties of starch to achieve maximum yield with lowest protein residues. Wet-milling is commonly employed to extract starch from millets. The starch can be isolated using aqueous, alkaline and acidic steeping methods by solubilizing protein residues. The millet flour was soaked in water and alkaline (sodium hydroxide and Sodium hydrogen sulfite) solutions. Aqueous steeping was carried out for 24 hours using distilled water while alkaline steeping involed soaking for 18-20 hours. Acid steeping was carried out using dilute sulphuric or hydrochloric acid solutions. Amongst all the steeping methods alkaline steeping produces high starch yield. The slurry is then rinsed and filtered several times to remove protein and fibrous part. The starch is isolated by centrifugation and dried.

Native or natural form of starch is not stable to processing due to their innate functional properties. The modified starch on the other hand has an edge over the native starch making them more suitable in terms of enhanced physico-textural and physico-functional properties for varied food products during processing. Modification of starch may be accomplished by physical (thermal or non-thermal), chemical (oxidation, esterification, etherification, cross linking, acid hydrolysis, acetylation), enzymatic (cyclodextrin

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glycosyltransferase, α-amylase, β-amylase, amylo-sucrase, amylo-maltase) and dual (combination of physical, chemical and enzymatic) techniques.

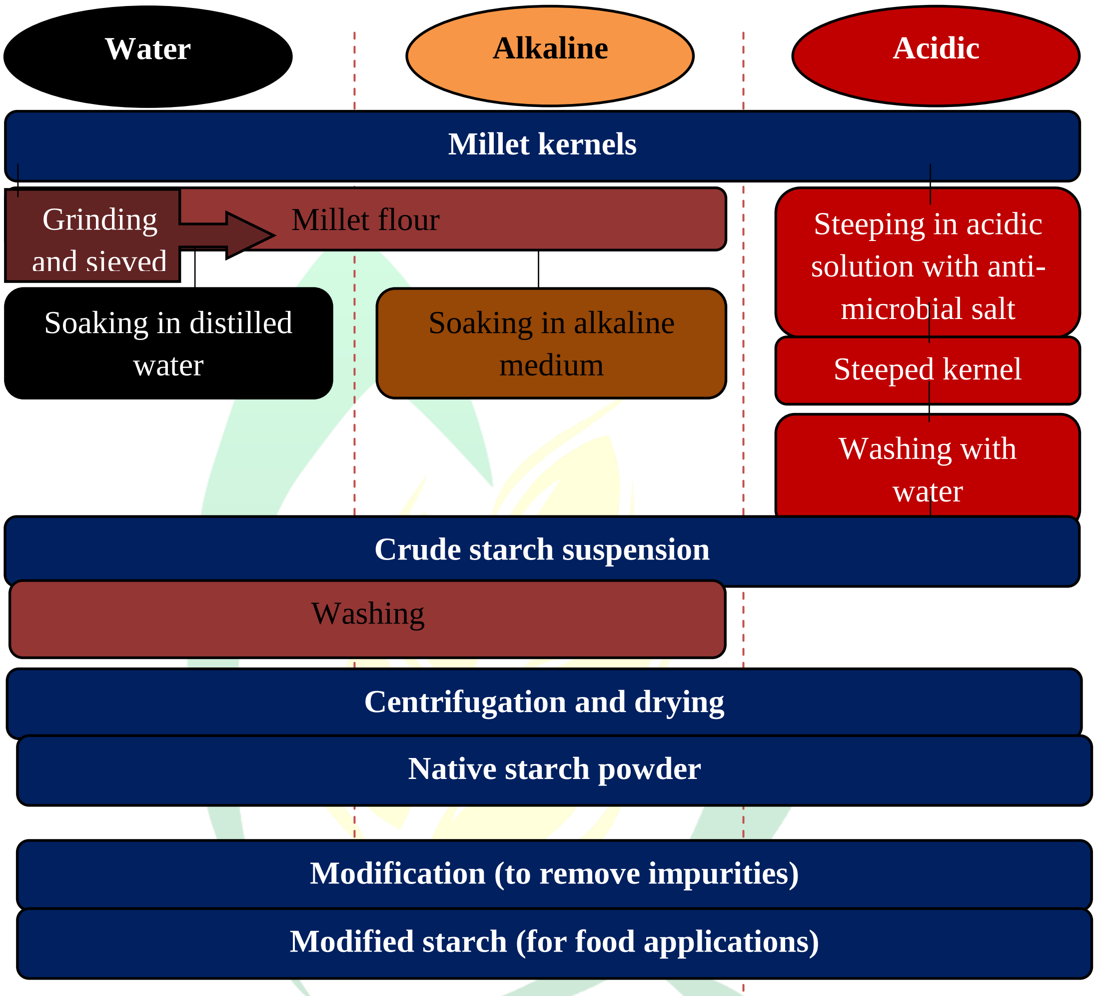

Figure 1 Isolation and modification of millet starch

Functional properties of millet starch

Swelling, solubility and water absorption capacity

Hydrothermal treatment is basically heat-moisture treatment resulting in physical modification of starch. It involves heating at high temperatures (84-120°C), above the glass transition temperature (Tg) but below the gelatinization temperature (To), while maintaining low moisture levels (35%) for a predetermined period of time. Annealing on the other hand is performed at a temperature above the glass transition but below the gelatinisation temperature of starch. For millet, 50 g of starch is treated with excess water at 50°C (T_g< 50°C < T_o) for 48 h. As a result, starch swells up by absorbing water.

Swelling power indicates the water holding capacity of starch, which is generally used to differentiate various types of starches. The swelling power of millets starch varies in the temperature range of 50 to 90ºC. Swelling power of pearl millet flour was found between 2.12 and 19.65 $g.g^{-1}$ at a temperature range of 55-95°C while for minor millets it varied between 14.72-18.83 $g.g^{-1}$ at the same temperature range.The swelling power of millet starch is lower than rye, wheat and potato starch indicating that the former starch granules are resistant to swelling owing to high intra and inter molecular bonding forces between them.

Solubility is one of the important physicochemical characteristics that determine the functional properties of starch. The amylose content and crystalline structure of the starch influences water solubility. Solubility of pearl millet starch ranges between 10-16% while for other millets namely barnyard, foxtail, kodo, little and proso millet it ranged between 14.9 to 25.8%.

The starch granules having short amylopectin chains may readily bind water molecules by hydrogen bonds. However, amylose and its lipid complexes and long amylopectin chain create helical boundaries that hinder the entry of water molecules and binding. Low amylose starches are widely used as thickening agents in varied food applications such as sauce, soups, gravies and custard etc as shown in Table 2. During heating, the water absorption index of millet starch flour is associated to swelling capacity. The water absorption index of millet starch ranges between 0.77-1.22 $g.g^{-1}$. The porous structure of starch polymers attributes to high water absorption capacity which aids in the preparation of baked products like bread and ready-to-eat breakfast cereals like pasta.

Pasting behaviour

Pasting properties of food depends on nature of starch, its composition, concentration, cooking and cooling temperatures, presence of solutes (sugar), lipid and pH. Pasting properties are determined using a Rapid Visco-Analyzer (RVA) and Brabender Visco-Amylograph that measures the viscosity of a sample while stirring over a given period of time. RVA measures the *peak viscosity* (viscosity reached due to increase of temperature after reaching the pasting temperature), *breakdown viscosity* (holding period at a constant high temperature when swollen granules rip or rupture), *setback viscosity* (viscosity increases again as granules are cooled and retrogradation is taking place) *and final viscosity* (viscosity continues to increase until a plateau is reached) at different phases of food preparation. Waxy starches have higher percentage of amylopectin and may instantly absorb water resulting into swelling up of granules. It results in achieving pasting temperatures in a very short span of time. The pasting properties of barnyard millet starch had the lowest breakdown viscosity (BDV) of 20 Brabender units (BU) with a peak viscosity of 375 BU, whereas the proso millet starch had the maximum peak viscosity of 520 BU and breakdown viscosity of 20 BU. The tendency of starch to retrograde after gelatinization and cooling is referred to setback viscosity (SBV). Pasting profiles of both barnyard and Kodo millet starch showed higherSBV than proso millets. The SBV can vary in different varieties with the same species. Pasting properties of starch are importantcriteria for studying their behaviour during processing, its use in food applications as well as in production of commercial resistant starches which can be used for therapeutic purpose.

Thermal properties

The gelatinization and pasting properties are mainly used to reflect the starch quality. Starch is gelatinized on moist heating and exhibit characteristic behaviour. Thermal properties of starch are popularly represented as peak temperature (Tp), onset temperature (To) and enthalpy of fusion (energy provided to change the state of starch from a solid to a liquid) and are measured using differential scanning calorimeter (DSC). Starch gelatinization is a process of breaking down the intermolecular bonds of starch molecules in the presence of water and heat. Gelatinization of starch show wide variation between different millets as well as between varieties of the same species. The amylose:amylopectin ratio and size of starch granules effects its characterization. The high gelatinization temperature of starch indicates more energy input required to initiate gelatinization attributing to the proportion of amylopectin crystals present in millet starch. The gelatinization temperature (To) of different millets namely proso millet (68.4°C)>foxtail millet (66.7°C)>finger millet (63.9°C)>pearl millet (62.8°C) show a descending order indicating that the millet starch is less porous and more compact for proso millet and takes more time to achieve gelatinization temperature as compared to pearl millet.The enthalpy (ΔH) of millet starches was found as finger millet (13.2 J/g)>proso millet (13.1 J/g)>pearl millet (12.3 J/g)>foxtail millet (11.8 J/g)indicates a stronger bonding in finger millet starch corresponding to the heat required to break the inter-molecular bonding.

Film forming

Millet starch can be used to prepare films that can be used as a packing material. The thickness of films depends on the granule shape and size, and the amylose to amylopectin ratio. Film forming properties depends on presence of moisture content. The moisture content in millet starch varies from 10.1% to 14.6%. The maximal percent of moisture content has been recorded in foxtail millet starch film. The insolubility in aqueous medium of millet starch denotes its integrity and water resistance in packaging materials. Higher water solubility may be valuable for the coatings of fresh and minimally processed foods. The thickness of the film relates to the mechanical strength and permeability of the film to gases and water vapours. The thickness of the films of millet starches varied from 0.11 and 0.15 mm with maximum value exhibited by little millet while the minimum was shown by finger millet. Opacity is used to determine the transparency of a film. A high value of opacity indicates lower transparency. The lowest opacity (1.75%) was observed for little millet starch films. Solubility of films is an essential factor for food packaging material. The solubility of the films ranged between 25.6 to 31.5%. The highest solubility value has been reported for the little millet starch film.

Table2 Functional characteristics and applications of millet starch

<table>
<tr><th>Starch</th><th>Modified/native starch</th><th>Characteristics</th><th>Application</th></tr>
<tr><td rowspan="2">Pearl millet</td><td>Native</td><td>Water holding capacity and swelling capabilities are enhanced and disintegrant efficiency was improved.</td><td rowspan="2">In the manufacture of chloroquine’s tablets as a disintegrantconsumablecomposite film</td></tr>
<tr><td>A mixture of starch and carrageenan gum</td><td>Increased carrageenan and starch concentrationsimproved film tensile strength while lowering water vapourpermeability in composite film.</td></tr>
</table>

	Succinylated and hydroxypropylated	Reduced syneresis and enhanced cold storage stability	White sauce
	Octenyl succinylate	Structural strength and high viscosity	Replacer of fat in low fat ice-creams
	Acetylate and hydroxypropylated	Enhanced flexibility, transparency and water solubility	Biodegradable starch film
Teff millet	Pregelatinized	Better compressibility and faster disintegration time	In the preparation of chloroquine phosphate tablet, as a disintegrant
	Native	Prevents lipid oxidation, has a strong mechanical and water barrier qualities and has a high radical scavenging action.	Camucamu extract-based antioxidant packaging material
Foxtail millet	Native	Antioxidant and antimicrobial properties in active packaging materials, UV light protection properties.	Packaging film containing clove leaf oil, for queso Blanco cheese
Barnyard millet	Native	Solubility in water, water vapour and moisture levels permeability have all decreased, light barrier and antioxidant properties.	Edible starch films having oil of borage seed

Finger millet	Oxidized and acetylated	In the instance of modified starch compacts, the reduction in disintegration deformability and time is offset by an increase in tensile and crushing strength.	Formation of a tablet and capsule

Conclusion

Starch is a key component of total carbohydrates present in millets. It is highly underutilized and its use in varied food applications needs to be explored for functional aspects like other commonly used starches such as viscosity regulator, texture modifiers, thickening and gelling agents. Native millet starch has limited functionality and needs to be modified for enhancing its physico- chemical, textural and bio-functional properties. The use of different processing techniques affects their behavioural characteristics which help in developing varied food products that are beneficial to health. This would not only benefit the individuals who consume millet as their main source of nutrients but also help the food scientists and food developers to formulate varied food products with enhanced physicochemical properties. In addition, in depth studies needs to be conducted on characterization of major and minor millets with respect to starch and their behaviour for significant applications in food processing sector.