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Review article

Application and functional properties of millet starch: Wet milling extraction process and different modification approaches

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A R T I C L E I N F O

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A B S T R A C T

In the past decade, the demand and interest of consumers have expanded for using plant-based novel starch sources in different food and non-food processing. Therefore, millet-based value-added functional foods are acquired spare attention due to their excellent nutritional, medicinal, and therapeutic properties. Millet is mainly composed of starch (amylose and amylopectin), which is primary component of the millet grain and defines the quality of millet-based food products. Millet contains approximately 70 % starch of the total grain, which can be used as a, ingredient, thickening agent, binding agent, and stabilizer commercially due to its functional attributes. The physical, chemical, and enzymatic methods are used to extract starch from millet and other cereals. Numerous ways, such as non-thermal physical processes, including ultra-sonication, HPP (High pressure processing) high-pressure, PEF (Pulsed electric field), and irradiation are used for modification of millet starch and improve functional properties compared to native starch. In the present review, different databases such as Scopus, Google Scholar, Research Gate, Science Direct, Web of Science, and PubMed were used to collect research articles, review articles, book chapters, reports, etc., for detailed study about millet starch, their extraction (wet milling process) and modification methods such as physical, chemical, biological. The impact of different modification approaches on the techno-functional properties of millet starch and their applications in different sectors have also been reviewed. The data and information created and aggregated in this study will give users the necessary knowledge to further utilize millet starch for value addition and new product development.

1. Introduction

Cereals play a significant part in the human diet owing to their ease of preparation, long shelf life, and distinct flavor. Millets are well-known cereal grains in the grass subfamily *Panicoide* [1]. One of the key restraints in any food product for a robust and healthy

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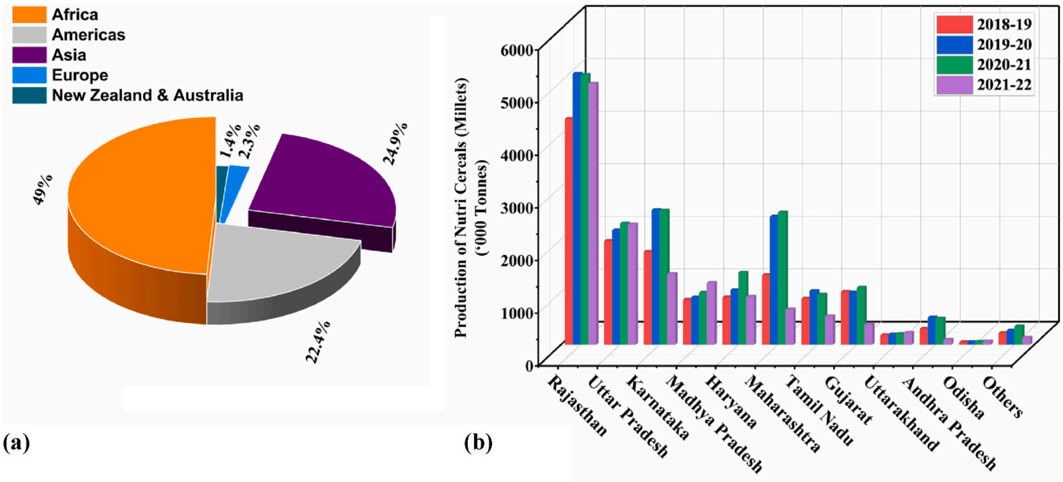

Fig. 1. (a)Global scenario of millet production (2019) (b) India state wise millets production (2018-22).

Table 1
Classification and general characteristics of different millets.

Name of millets	Origin country	Physical/visual appearances			References
		Color	Size	Shape	
Major millets					
Pearl (*Pennisetum Glaucum*)	West Africa	Grey, pale yellow and brown	3–4 mm long	Ovoid	[18,19]
Finger (*Eleusine coracana)*	Uganda	Brown (light/dark)	1–2 mm dia.	Spherical	[21,146]
Sorghum (*Sorgum bicolor)*	North Africa	Yellowish and brown	2–5 mm dia.	Spherical	[147]
Foxtail (*Setaria italic)*	China	Pale yellow and orange	2 mm long	Ovoid	[20]
Proso (*Panicum Miliaceum)*	Asia	Creamy, yellowish and orange	3 mm long & 2 mm dia.	Spherical to oval	[148]
Minor millets					
Kodo (*Paspalum Scrobiculatum)*	India and Africa	Dark brown	1.2–9.5 μm long	Elliptical to oval	[149]
Barnyard (*Echinochloa Crusgalli)*	India and Japan	Light brown and white	2–3 mm long	Tiny round	[1,150]
Fonio (*Digitaria iburua and Digitaria exilis)*	Africa	White, pale brown or purplish	1 mm	Oblong to globose	[151]
Teff (*Eragrostis tef)*	Ethiopia	Light brown	0.9–1.7 mm long & 0.7–1.0 mm dia.	Oval	[152,153]
Little (*Panicum Sumatrense)*	Asia	Grey to white	1.8–1.9 mm long	Elliptical to oval	[154]
Browntop (*Brachiaria or Urochloa ramose)*	South Asia	Tan white and greenish	4–5 mm long	Ellipsoid	[155]

lifestyle at the consumer's end is the product's nutritional eminence [2,3]. The low yields of major crops, such as wheat, rice, corn and others, are negatively impacted by the current socio-economic and ecological issues. This factor also had a negative impact on local agricultural growth, decreasing grain output; accelerate high food prices and significant global food safety challenges [3,4]. In addition, due to a lack of resources, local farmers struggle under these precarious conditions. Therefore, novel technology must address the problems with on-field restricted production to find a suitable cereal crop that may serve as an alternative food source and effectively reduce and ease the burden of the significant cereal crops [5,6]. A nutritious and dietary fiber-enriched food alternative concerning important cereal crops is millet [7]. As a primary cereal crop in the tropical and semiarid regions of Asia, Africa, and the Middle East, millets have a lower vulnerability to adverse weather conditions and a higher yield on marginal land [4–8]. Millets possess excellent amounts of macro and micronutrients, and their importance in the agro-industrial sector is receiving much scientific attention [8]. Millets aren't widely available for commercial production and consumption due to dearth of agricultural space, public awareness, and the small size of these grains compared to other common grains [9,10]. Their total annual production is 2715 million tonnes in their typical growing zones, including drier parts of Africa and Asia. Fig. 1(a) graphically shows the Global (1a) and India (1b) scenario of millet production between the years of 2018–2022. As the figure showed that, African continent contribute major share in millet production, with 423 lakh tonnes, followed by America (193 lakh tonnes) [11,12]. Asia is the 3rd main producer of millet globally (215 lakh tonnes), whereas India is the most significant contributor (80 %), followed by China (20 %) of the total production [8–12]. The UNGA (United Nations General Assembly) declared 2023 as the International Year of Millets (IYoM) on March

5, 2021, after a motion promoted by India and supported by 72 nations. The Indian government will commemorate IYoM 2023 to promote Indian millets, recipes, and value-added products worldwide. India's millet state-wise details from 2018 to 22 are also presented in Fig. 1(b). In India, Rajasthan, Uttar Pradesh, and Karnataka are the top three Indian states for millet production [11–14]. Additionally, millets are referred to as "poor men's crop" and consumed globally in the form of chapati, bakery goods, idli, chiwada, flakes, rava, beverages, uppma and kitchadi and others due to containing the excellent amount of micro nutrients, dietary fibres, resistant starch, polyphenols, antioxidants and other health beneficial bioactive compounds [15].

Millets are classified into different varieties based on their colors, shapes, and sizes. The small-seeded, round-shaped millets belong to the *Poaceae* family and are the earliest and most likely first domesticated cereal grains humans predominantly employ for native purposes. Millets are generally found in two forms, major and minor millets in nature. The major millets include pearl, sorghum, finger, proso, and foxtail millets. However, the minor millets comprise little, barnyard, kodo, teff, fonio, and browntop (Fig. 1) [16,17]. Table 1 summarizes the main characteristics and classifications of different major and minor millets. Millets are abundant sources of lipids, polyphenols, vitamins, dietary fiber, and minerals. Millets possess reasonable amounts of nutrients such as carbohydrate content (60–70 %), fat content (1.5–5 %), protein content (6.9 %–19.9 %), fiber content (12.9 %–20.0 %, and minerals contents (2.4 % and 4.0 %) respectively [17–19]. In addition, the nutritional value, mineral content, bioactive compounds, and others depend on the types and varieties of millet. The higher amounts of nutritional characteristics and gluten-free nature of millet are responsible for its widespread acceptance and consumption [20,21]. In contrast to wheat and rice grains, millets have higher nutritional values, which make them an effective food alternative for curing diseases like diabetes and celiac. Malnutrition due to nutritional deficiency can be cured by fortifying millets with staple cereal crops [18,22].

Millets can be used to develop several types of value-added food products such as drinks, cuisines, soups, sauces, ice cream, non-alcoholic beverages, porridge, ready-to-eat meals, confectionery, bakery goods, beer, and non-fermented foods (flatbreads and tortillas) due to their higher nutritional and functional attributes [3,23]. Despite millet's good nutritional and functional attributes, it also contains good starch composition with qualities and interactions of its primary component [4,8,24]. Based on the hydrolysis of α-amylase, the starch has been classified as rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS). Additionally, resistant starch generates a feeling of fullness as it avoids digestion, moving into the colon where it undergoes fermentation, acting as a prebiotic for beneficial bacteria involve in digestion process. The millets are highly preferred for application due to the significant proportion of resistant starch [2,8,24]. The small granules of starch are secluded through discrete techniques like enzymatic, physical, and chemical, which include gravity sedimentation, filtration, and centrifugation, which are further utilized for developing discrete food products for food and non-food production [25]. Starches do not always possess the physical and chemical qualities essential for their intended uses in their natural condition.

However, their modification enhances multiple functional properties that make them appropriate for commercial use in the food and non-food industries [26,27]. There are several types of thermal and non-thermal techniques, such as physical, chemical, biological, pre-gelatination, and heat moisture treatment, are used for the modifications of starch to improve their physico-chemical and functional properties, such as imparting thermal stability and decrease retrogradation. In this regard, the non-thermal techniques of starch modifications are emerging innovative techniques, gaining more importance due to their eco-friendly sustainability and use of low energy [28]. Barbhuiya et al. [29] reviewed and reported that the non-thermal techniques are one of the innovative emerging techniques; that can be replaced by the thermal processing technologies, which improved the structural components of food and food products with desirable functionality. Numerous types of non-thermal techniques such as high-pressure processing, ultrasonication, cold plasma, pulsed electric field, and gamma-irradiation significant attempts have been undertaken in recent years to modify the structure and other properties of starch [28,30]. This research is essential to logically creating food items based on starch with enhanced characteristics [31]. The present study aimed to assemble the details about the millet starch, its modification procedures, and its functional properties. The influence of the different factors on the hydrolysis of the starch and the applications of the modified starches in various sectors are also reviewed. Other data-based such as Scopus, Google Scholar, Research Gate, Science Direct, Web of Science, and PubMed were used to collect literature between the years of 1993 and 2023 for detailed study using keywords such as millet, millet starch, extraction and modification, and their health benefits and applications. The data and information created and aggregated in this research study will give users the necessary knowledge for optimal millet starch utilization for value addition and new product development.

2. Millet starch

Starch is the most abundant polysaccharide found in nature, followed by cellulose; it is cost-effective and considered an indispensable energy source due to the presence of amylose and amylopectin components [32]. It contains 20–30 % of starch granules in amylose and 70–80 % of granules in amylopectin, respectively. Amylose components of starch are linked with alpha-1, 4 glycosidic bonds, whereas amylopectin is linked with alpha-1, 6glycosidic bonds [33,34]. Several renewable sources, such as plants, including cereals, green fruits, and tubers, are the primary sources for producing starches. Therefore, starch is the millet grains' principal constituent, accounting for approximately 70 % of the total grain [17]. The starch granules of millets generally vary from small to large and can be spherical, oval, and polygonal in shape [35]. Millet starch is widely used in the food and pharmaceutical sector as a swelling agent, ingredient, thickening agent, emulsifier, gelling agent, binding agent, etc., due to its unique and hypoglycaemic properties compared to other cereal starch [36,37]. Furthermore, wet milling methods such as water, alkaline, and acidic are used to isolate and extract starches from millet and cereal grains.

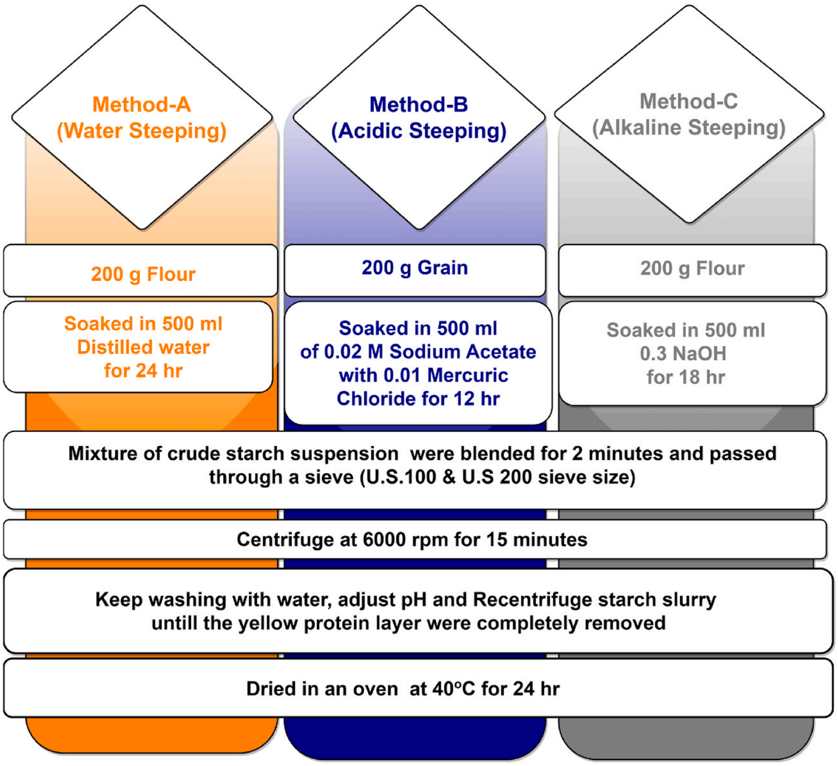

Fig. 2. Wet milling starch extraction methods.

3. Wet milling process of starch extraction

Numerous procedures and chemical reagents are employed to dissolve the protein component and extract starch from grains, as starch granules are closely attached to the protein matrix of grains [38,39]. Starch's physicochemical and functional characteristics vary depending on the source and extraction method utilized. Typically, millet starches are obtained through one of three wet milling processes, where the flour or millet grain are soaked or steeped in water, an aqueous solution, or acidic and alkaline mediums. This process helps to separate the starch form other constituents of millets [40,41]. Fig. 2 comprehensively summarizes the different wet milling extraction techniques and their procedure. The wet milling starch extraction procedure such as water, alkaline, and acidic steeping are often used to extract starch. There are merits and demerits associated with each approach; nonetheless, a precise process with high yields and minimal residual protein content is essential [41,42]. Starch extraction typically involves anatomic fragmentation, cell breaking, and final starch purification. The millets' physicochemical composition and functional properties determine the genre of chemical solution for starch extraction. Palacios et al. [43] studied that, the effects of alkaline or acidic treatments on the techno-functional, physical and chemical characteristics of corn starch. These isolation techniques affect starch granules amylose concentration, crystallinity, and enthalpy. The scanning electron microscope results confirmed that the isolation technique changed the surface of starch granules. In certain instances, there were holes on the surface of starch granules, which were altered due to the presence of protein bodies. The starch yield obtained using the steeping technique was reported at 51.03 %, and the lowest (39 %) was reported with the acid steeping method. Therefore, alkaline stepping eliminated the majority of protein from the sample.

In contrast, the approach of water steeping produced a sample with more excellent protein content due to the solubility of protein bodies dispersed equally throughout the endosperm between starch granules in certain solvents. Nyakabau et al. [44] also investigated the effects of steeping solution on the extraction yield and quality of zein starch; they reported that the alkaline steeping process yielded a starch that is low in protein and lipids but high in amylose. The fact that zein is insoluble in alkaline solution must also be considered. This is because soaking in alkaline solutions softens the protein–starch matrix, which can then be separated by centrifugation. Nonetheless, the zein in protein bodies is insoluble in water [45]. Comparing the alkaline and acidic steeping methods, the granules produced by the acidic steeping method had a more significant protein residual (4.3 %) than the alkaline steeping (0.7 %) method. The Alkali isolation approach is said to be the most popular method since it makes it simple to remove any related and associated proteins [46,47].

4. Physicochemical properties and structural composition of millet starch

Starch, lipids, protein, vitamins, dietary fiber, and minerals are among the primary and significant components that make up millet

Table 2
The comprehensive nutritional profile of millet starches.

Millet starch	Starch yield (%)	Amylose content (%)	Protein (%)	Fat (%)	Ash (%)	Moisture content (%)	References
Major millet							
Pearl	39.40	4.96	0.53	0.38	0.10	12.47	[18,48]
Sorghum	–	21.5	0.28	0.24	0.19	–	[35]
Finger	52.54	21.51	1.45	0.25	0.32	–	[156]
Foxtail	69	32.0	–	–	–	–	[157]
Proso	54.1	28.51	1.21	0.27	0.62	9.86	[8,18]
	93.7	33.9	–	–	–	–	
Minor millet							
Kodo	93	19.61	–	–	–	–	[158]
Barnyard	65.70–66	15–20.02	–	–	–	–	[48,135,150]
	39	21.27	1.77	8.57	0.84		
Fonio	32	22.26	0.3	2.6	0.8	15	[8,18]
Teff	–	17	0.01	0.52	0.41	8.26	
Little	–	18.81–32.06	–	–	–	–	[8,48]

Table 3
Morphological characteristics of different major and minor millet starches.

Millet Starch	Shape and size of starch granules	References
Major millet		
Pearl	Polygonal, small spherical granules & 3.5–23 μm size	[68,159]
	Round and oval & 3–12 μm size	[160]
Finger	Irregular, spherical shaped & 5–15 μm size	[160]
	Polygonal & 2.5–17 μm size	[24]
Foxtail	Polygonal, spherical & 2.5–24 μm size	[48]
	Spherical, polygonal, & and 50 μm size	[161]
Proso	Polygonal, oval, spherical & 3–15 μm size	[48]
	Even round & 5–15 μm size	[112]
Minor millet		
Kodo	Minor spherical and polygonal & 1.0–9.0	[48]
Barnyard	Polygonal, spherical & 3–10 μm size	[48]
Fonio	Polygonal & small in size 8 um	[162]
Teff	Polygonal-shaped granules & 2–6 mm size	[163]
Little	Big polygonal and roughly spherical & 8.09 μm size to 19.05 μm	[55]
	Spherical, polygonal, and rhombic & 1–9 μm size	[17,48]

as an extensively nutritionally enriched cereal grain [3]. Specifically, mineral contents such as magnesium (Mg), manganese (Mn), and phosphorus (P) also exist in greater abundance in millet as compared to cereals. Starch comprises around 51 % to 79 % of the composition of millet, which is one of the most significant constraints in millet. Starch primarily consists of two constituents: amylose and amylopectin [47]. In millet starches, amylose content generally ranges from 20 % to 32 %, which enhances its hypoglycaemic characteristics [58]. The inclusion of additional constituents as impurities within the starch granules notably impacts both its functionality and versatility for various applications.

The total lipid content of millet starch comprises 89 % of polar phospholipids and 11 % of non-polar phospholipids [47,48]. This indicates that polar phospholipids are the predominant lipid found in millet starch. Due to their hydrophobic connections and cohesive nature, these lipids form complexes with the amylose which impairs the swelling capacity and flow ability of the starch [50]. Proteins include hydrophilic and hydrophobic links, influencing- and oil-binding capabilities. Fibers have been shown to reduce the amount of oil that may be absorbed and reduce the ability to bind oil [18]. Polyphenols have yet to be studied for millet starch functionality. A variety of physicochemical characteristics may be affected by adding polyphenols from an external source to starch, and this has been extensively studied, such as the addition of pomegranate peel extract, green tea, Chinese hawthorn, and Chinese gall extract in wheat starch for enhancing its peak viscosity [51]. The proportion of yield, amylose concentration, and chemical composition of millet starch varies significantly across millet varieties and starch extraction methods. Amylose is vital to the functioning of starch, where its proportion in the millet species varies significantly. Based on the previous literature, the highest amylose content is possessed in proso millet and the lowest in pearl millet based on the earlier investigations. The nutritional and functional properties of different major and minor millets are depicted in Table 2. The amylose content of millets might indicate how well they work in the production of particular food items [8,50].

One critical parameter to define the molecular structure of millet starch molecules is the length of the starch chain (chain length). The features of starches that are affected by branch chain length include gelatinization, retrogradation, and pasting [18]. The amylose fraction of millet starch can be categorized into short and long-chain amylose by gel permeation chromatography. Pearl and finger millets contain larger quantity of long-chain amylose as compared to other millets. The α 1,4 and α 1,6 glycosidic bonds of pearl millet starch has chains of 8–21 glucosyl units in which the interior and exterior chain lengths are 5.0–6.2 and 12.0–13.8, respectively [52].

Starch also plays a vital role in food gelatinization. Starch gelatinization occurs when starch and water are heated, causing the

Fig. 3. Functional properties of millet starch.

starch granules to expand. This gives food a translucent and viscous texture. Water and heat break down the intermolecular connections of starch molecules, allowing the hydrogen bonding sites to engage additional water in starch gelatinization [50]. The gelatinization temperature of starches increased with the increase of the branch chain length. The starch gelatinization time is slashed as their amylopectin concentration rises [52].

The starches come in a wide variety of species, each with a unique morphological granule size. Native starch granules exist in much morphology like round, polygonal, oval flat, lenticular, kidney-shaped and elongated. Starch granules range in size from submicron to 100. Millet starch granules are primarily polygonal and spherical, with certain exceptions. The treatment or modification of millet starch significantly impacts its shape. The position of starch granules in the endosperm and the various environmental conditions also affect the morphology of starch since species growing at high elevations have bigger granule sizes [17]. Table 3 summarizes the morphological properties of the different types of millet starch reported by previous researchers.

5. Functional properties of millet starch

The key properties of millet starch includes functional attributes such as swelling capacity, solubility index, heat stability (degree of gelatinization) viscosity, digestibility, rheology, and structural properties (Fig. 3) [53–55]. These properties, directly and indirectly, impact the quality of foods and their applications at industrial scales for new product development, food, medical, and packaging sectors [56].

5.1. Pasting profile of starch gel

Pasting properties of the starch gels narrate the changes in starch-water systems during gelatinization and granule rupture under regulated temperature profiles and shear pressures. The viscosity of starch suspensions is utilized for evaluating the pasting characteristics during heating and cooling. The paste viscosity of starch granules reaches a maximum during heating. Then, it decreases with further heating, but the viscosity of starch paste rises with time during cooling, which is suggestive of starch retrogradation [57,58]. The different types of factors such as starch concentration and its composition (amylose content, amylose to amylopectin ratio), cooking and chilling temperatures, as well as the presence of solutes including lipids, sugars, and pH, are responsible for the influence of the pasting properties of starch [59,60]. Rapid-Visco Analyser is the most general technique used to regularly examine starch pasting properties such as viscosity breakdown, temperature, setback, and ultimate viscosity [54,61]. Based on the previous reports, it can be concluded that the proso millet starch showed the highest peak and breakdown viscosity.

Table 4
Pasting behavior of native and modified millet starch gels.

Millet	Modification Treatment	Pasting temp. (°C)	PT	PV	BV	FV	SV	HV	References
Finger	NS	63.6	–	4380	168	6120	2496	4212	[164]
	NS	64.35	–	3666.9	1828.9	4526	26,880	–	[165]
Foxtail	NS	81.6	–	2254	603	2734	1083	1651	[57]
	UMS	80.9	–	2412	812	2658	1058	1600	
	HTMS	82.5	–	1877	379	3095	1597	1498	
Pearl	NS	70.4–71		1860–3071	967–1248	1430–2961	437–1994	837–1900	[58]
	HTMS	–	4.835	2337	1356	5460	4480	980	[54]
Proso	HTMS	83.9	–	2290	320	3210	1250	1960	[62,63]
	NS	76	–	2822	1470	1470	501	967	
Little	NS	95.0		2597.67	1426.1	3046.6	1893.11	1153.56	[55]
Teff	NS	72.1–74.8	4–9.4	3072–3492	756–1200	3072	1056	–	[163]

Where; NS (Native starch) HTMS (Hydrothermaliy modified starch), UMS (ultrasound modified starch).

In contrast, the barnyard millet starch had the lower peak and breakdown viscosity compared to other millet starches [17,62]. The pasting properties of the starch may depend on several factors, such as types of cultivars, size of starch granules, and amylose and phosphorus content of the starch granules. Therefore, a higher amount of phosphorus is responsible for the increased hydration ability of starch after gelatinization, which results in higher viscosity and gel formation capacity. Apart from its numerous uses as thickeners and gelling agents, the pasting capabilities of starches are essential for developing commercially resistant starches [63–65]. Table 4 summarizes the previously reported pasting behavior of native and modified millet starches.

5.2. Swelling capacity and solubility

Starch granules expand by absorbing water when exposed to water and heat. Amylopectin is primarily accountable for the swell of starch granules and the rise in viscosity upon heating. However, α 1,4 glycosidic linkage interlaced with α 1,6 glycosidic linkage and restricts starch granules' swelling [17]. In the temperature range, 50 °C and 90 °C millet starches demonstrate swelling power. The swelling power capacity of millet starches varied from 14.43 to 18.83 g/g, and their solubility ranged from 14.9 % to 25.8 %, respectively. There is a correlation between amylopectin and the swelling power of starch granules, and a larger swelling is connected with increased water absorbance by α 1,4, and α 1,6 glycosidic bond. The amylose leached during heating is often known as the solubility power of starch, which is influenced by granule size and starch component [53,66]. The influential factors affecting solubility include crystalline arrangement, the magnitude of gelatinization, morphology, and granule size. In millet starch, the amylose concentration, swelling power, and solubility ranges are 11.57 %–21.93 %, 11.11 g/g to 17.91 g/g, and 12 %–15.20 %. Millet starches expand less than potato and wheat starches, which show that they have more vital bonding forces among the granules, making them more resistant to swelling [17,66,67].

5.3. Freeze-thaw stability

The freeze-thaw (FT) stability for starch, mainly millet starch, is determined by the quantity of water that separates from the starch gels (syneresis) during freeze-thaw cycles [68]. Freeze-thaw stability relies on the quantity of water, starch content, molecular structure, and heating history of the starch. A less proportion of α 1,4 glycosidic linkage and higher proportion α 1,6 glycosidic linkage might enhance FT stability of starches. Wheat and maize starch outperformed pearl millet starch in an FT stability test. Millet starch other than pearl millet has yet to be used in food composition because of a lack of literature on the freeze-thaw stability of millet starch [69,70].

5.4. Textural profile

Textural characteristics of starch gels are crucial for evaluating the performance of starch in food systems. Several variables influence the formation of starch gel, including the concentration of starch, the kind of starch, modification, cross-linker, and the duration of time and temperature. Non-waxy starch pastes change into a solid gel of three-dimensional networks during retrogradation, while waxy starch pastes produce a soft gel of aggregates [17,71]. Generally, greater amylose concentration is related to stronger starch gels. Amylose-based networks provide starch gel's elasticity and resistance to deformation, while soft gels containing aggregates exhibit increased penetrability, stickiness, and adhesion. The initial hardness of a starch gel and the stickiness and digestibility of processed food are determined by amylose retrogradation [17,71,72]. Texture profile analysis (TPA) is the most generally utilized technique for inspecting and assessing the textural features and characteristics of starch gels and starch-based food products. The compressive force is applied twice cyclically to the sample during the TPA test, and five critical properties of the gel are measured as a result: hardness, cohesiveness, adhesiveness, tensile strength, and brittleness. A substantial factor in the categorization of starchy foods is starch gel hardness, which has a direct link with starch content. Natural gels are often weak, but the desired texture may be created by adding an external gelling agent or by changing the native starches; for instance, the addition of guar gum and its hydrolysate significantly improved the textural properties of pearl millet starch gels. The use of modified pearl millet starches in gel formation resulted in substantial modifications in the textural qualities of the gels [71,72]. The conversion of starches enhances their ability to absorb water, making a soft gel hence, the assortment of an acceptable starch and its modification process depends on its intended application.

5.5. Starch retrogradation

Starch tends to thicken and make rigid gels when exposed to heat, a process known as retrogradation. The amylose and amylopectin molecules in the gelatinized starches interact with one another and with water to recrystallize when the starches are cooled, creating a more organized structure than previously [73–77]. The several factors such as the quantity of water, concentration and size of starch granules, presence of other components (fibers, lipids and proteins), and storage time and temperature, affect the retrogradation process. Starch with short α, 1,4 glycosidic linkages are highly prone to recrystallization [75,77]. The morphology of the starch particle directly impacts retrogradation, as small granules are the most susceptible to retrogradation, while larger granules are the most durable. Comprehending the concentrations of amylose and amylopectin and their effects on starch retrogradation is valuable in choosing suitable starch for specific food uses [70–77].

5.6. Starch digestibility

The digestibility of starch is an essential nutritional parameter that influences its acceptability to consumers. Starch digestibility in foods is proportional to the quantity of easily digested starch [78]. Millet flour has lower in-vitro enzyme digestibility ratings than wheat flour because of its poor enzymatic susceptibility and strong enzyme resistance. The higher starch digestibility level has been reported in wheat flour and its products [78–84]. For example, with the addition of millet flour, the amount of readily digested starch in millet-based chapatti falls from 32 % to 30 % in vitro. According to Sharma et al. [85], pearl millet starch contain highest amount of resistant starch (RS). This suggests that various constituents (lipid and protein) may affect the digestion of starch with enzyme accessibility to starch molecules. Finger millet flour exhibited limited starch digestibility and a low glycaemic index. Removing fats and proteins from millets significantly improves in vitro starch digestibility and glycaemic index. Additionally, extra components, species type, and starch treatment or alteration impact the digestibility of millet starches. In vitro enzyme digestibility was reduced by 60 % in millet flour independent of the amount of pre-gelatinized starch. This may be attributed to increased phenolic compounds (tannins, ferulic, and coumaric acid) in millet flour [78]. The biscuits made from germinated finger millet and groundnut flour enhanced in vitro slowly digestible and resistant starch, total phenolic content, and antioxidant activities, whereas rapidly digestible starch, glycaemic index, and phytic acid, starch hydrolysis index decreased [86].

The processing technique such as fermentation, germination, malting, blanching, frying, popping, toasting, puffing and baking are potential to improving the digestibility of millet starch includes. These processes enhance enzyme susceptibility but also decrease the RS content in millet [17,85]. Numerous of these approaches are regularly used daily and may also aid those who rely on millet or a low-calorie diet [17,86,87].

6. Hydrolysis of millet starch

The hydrolysis of starch is the test that is used to examine the genre and identify bacteria. The enzymes a-amylase and oligo-1,6-glucosidase are employed in this test to identify bacteria that can hydrolyse starch (amylose and amylopectin) utilizing the enzymes. Numerous variables influence the rate and degree of starch hydrolysis, which includes a ratio of amylose to amylopectin, starch-lipid complex, fiber and polyphenols, shape and size of starch granules and processing techniques [87,88]. The granules of millets are typically structured in a polygonal way with few minor spherical granules; apart from that, the presence of pores and pin-holes are also exhibited by some granules that aid the hydrolyzing enzymes for entering into the starch granules [89]. There are three primary constituents in glycaemic characteristics of millet, namely starch, lipid, and proteins. Inhibitors such as amylase, anti-nutrients (phytates and tannin), fatty acids, and starchy characteristics also affect the hydrolysis of starch. Compared to saturated fatty acids, unsaturated fatty acids have a more significant impact in slowing down the rate of starch hydrolysis [90]. The interplay of carbohydrates, protein, and lipids impacts how easily they may be digested, and it has been shown that removing proteins and lipids dramatically increases the glycaemic index [90,91]. Numerous types of research have reported the impacts of the polyphenols, fiber, and lipid contents on the hydrolysis of starch.

6.1. Effects of different factors on hydrolysis of millet starch

6.1.1. Polyphenols

Polyphenol contents are prevalent in millet, and their compositions vary depending on the species. The millet contains mainly phenolic acids with minor amounts of flavonoids [92]. The phenolic and flavonoid groups inhibit - glucosidase and pancreatic-amylase noncompetitively and, in certain instances, competitively [93], which resulted in a decrease in postprandial hyperglycaemia and can also be used in the development of novel anti-diabetic foods [94].

6.1.2. Lipid contents

Lipids can reduce the pace of enzymatic starch breakdown by forming complexes like amylose-lipid complexes (ALC) with free fatty acids. This interaction lowers the rate of starch hydrolysis and subsequent digestion [95]. Amorphous area hydrolysis, occurs first,

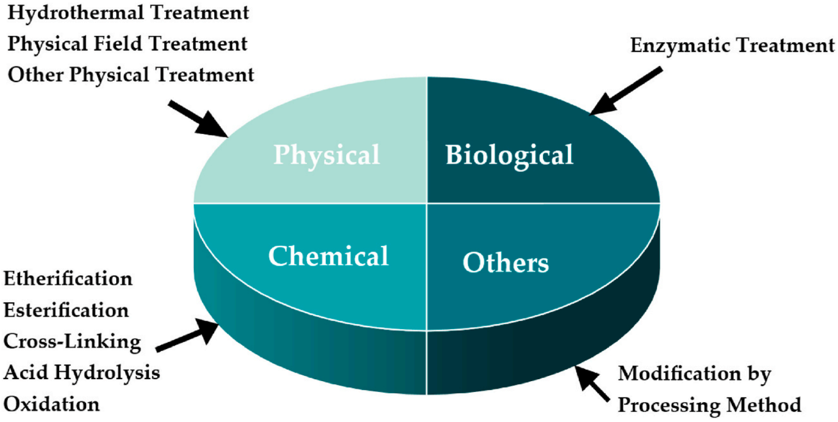

Fig. 4. Different Modification approaches for millet starch.

followed by the gradual destruction of amylose inclusions. Most millet fatty acid makeup comprises the three most common fatty acids: palmitic, oleic, and linoleic acid [96]. The composition of starch with C12 (lauric acid) and C18 (oleic acids) have lower hydrolysis rates. Still, the rate of enzymatic hydrolysis was not substantially reduced when starch and linoleic complexes were combined. This can be linked to the instability of the linoleic-starch combination. Lipids with varying degrees of unsaturation demonstrate various influences on the rates of starch hydrolysis and their complexes. Long-chain emulsifiers' starch digestibility was lower than short-chain emulsifiers [91].

6.1.3. *Fiber contents*

The millets contain a higher amount of fiber than the other cereals. Millet possesses approximately 7–21 % dietary fiber, comprising of soluble and insoluble fiber fraction of 2.5 % and 19.5 % respectively. Fiber increases the digesting mixture's viscosity, lowering the enzymatic starch hydrolysis rate. Millets contain resistant starch, which adds to their dietary fiber and provides a variety of health advantages when consumed in moderation [97,98]. The benefits of RS include avoiding fat build-up, decreasing blood glucose and cholesterol levels, preventing colon cancer, and reducing gallbladder stone development [24,78,82].

7. Modification approaches for millet starch

Starch is also one of the most plentiful bio-renewable elements, the planet's second-largest biomass after cellulose. Starch's exceptional capacity for quick and efficient modification, positions it as one of the most crucial and sought-after components for both food and non-food applications. Native starch is utilized as a texture stabilizer and conditioner in food systems. Still, its usage in industrial applications is limited due to its functionality as compared to the modified starch [26,49]. Native starch has some inherent properties such as instability to thermal, high hot-paste viscosity and shear stress, and a tendency to degrade rapidly in conjunction with low stability when kept in cold storage as well as weak resilience to acid, shear, and high temperatures, it is responsible for the deterioration of product quality and makes it less acceptable for widespread use in the food processing sector [99]. Native starches are modified to overcome these shortcomings that prevent them from being used in industrial applications [100]. Modifying native starch helps improve its functional properties by extending shelf life and increasing its use in papermaking, pharmaceuticals, medicine, food, and other non-food sectors.

Additionally, the food industry makes extensive use of modified starches for a variety of purposes, including imparting a thickening and gelling effect, as a stabilizer, for the preparation of edible coatings, for the encapsulation of food coatings, to retard retrogradation, for fat substitution, and to amplify resistant starch content [34,101]. The modification of starch is accomplished by physical, chemical, enzymatic, genetic, or a combination of these methods. Fig. 4 indicates the various modification approaches of native starch. Furthermore, non-thermal physical modification of starch alters its functional, structural, and physical properties, including crystallinity, heat stability, viscosity, stability solubility, and swelling capacity [99–101].

The physical modification includes hydrothermal treatment (heat and annealing treatments), physical field treatments (ultrasound, pulse electric field, irradiation, microwave, and ultra-high pressure), and other physical treatments (extrusion, cold plasma, drum-drying, milling, and freeze-thawing). Whereas, oxidation, etherification, esterification, cross-linking, and acid hydrolysis are some of the chemically based starch modification methods. Apart from that, the enzymatic and processing-based methods (roasting, puffing, and frying) are two more methods of starch modification [31]. The enzymatic modification comprises the development of a starch with an entirely different structure. Enzymatic reactions change the molecular mass, branch chain-length distribution, and amylose/amylopectin ratio of gelatinized starch. These changes occur when the enzymes react with gelatinized starch. Physical, chemical, and enzymatic modification techniques on native starch address the shortcomings and expand starch utilization in various food and non-food industrial applications. Based on the previous literature, the effects of different modification approaches on millet starch's physicochemical and functional properties are depicted in Table 5. Several researchers recently attempted starch modification to

Table 5
Effect of modification on techno-functional properties of millet starches.

Millet starch sources	Native/ Modified starch	Solubility (g/g) 60–90 °C	Swelling power 60–90 c	Water binding capacity (g/g)	Starch digestibility (%)			References
					RDS	SDS	RS	
Pearl	NS	16.09	3.80	291.8	–	–	–	[46,68,75, 166]
	CLS	–	–	–	46.1–50.6	34.5–36.4	13.6–19.4	
	NS	–	–	–	11.3–12.2	7.9–9.0	1.4–2.2	
	NS	–	–	–	46.3–51.6	37.2–38.7	12.0–16.5	
	EMS	14.17	3.77	258.2	–	–	–	
	HTMS	17.08	4.26	310.8	–	–	–	
Finger	NS	14.85	3.53	256.9	–	–	–	[68,108]
	NS	–	–	128.35–298.46	–	–	–	
	EMS	16.94	3.18	199.9	–	–	–	
	AMS	10.70	3.45	282.6	–	–	–	
	HTMS	13.40	3.49	290.8	–	–	–	
Foxtail	NS	–	–	–	35.7–39.1	45.7–53.0	11.3–15.7	[67,138]
	NS	–	–	–	70.38.20	11.42	18.20	
	AMS	–	–	–	41.53	16.15	42.32	
	AUMS	–	–	–	62.29	8.07	29.64	
	UMS	–	–	–	70.64	9.22	20.14	
	UAMS	–	–	–	40.57	13.84	45.59	
Proso	NS	34.88	24.99	138.43	–		–	[62]
	AMS	86.17	21.26	108.13	–	–	–	
	HTMS	12.45	10.37	191.65	–	–	–	
Kodo	NS	21.6	7.06	0.84				[80,167]
	NS	–	–	–	37.23	33.23	21.83	
Barnyard	NS	24.67	–	–	–	–	–	[135,168]
	CL	0.66–13	1.12–15	–	–	–	–	
Little	NS	–	3.22–9	1.37	25.92	–	–	[55]
Fonio	NS	0.8–15.1	2.2–35.9	–	–	–	–	[162]

Where; NS (Native starch) AMT (Acid Modification) HTMS (Hydrothermaliy modified starch), UAHT (ultrasound-assisted hydration), Dual modification: Annealing and ultra-sonication (AUS) Or ultra-sonication and annealing (UAS), HMT (Heat moisture treatment),EMS(Enzymatically modified starch)CLS(Cross-linked Starch), SP, swelling power; WBC, water binding capacity; RS, resistant starch; RDS, rapidly digestible starch; SDS, slowly digestible starch.

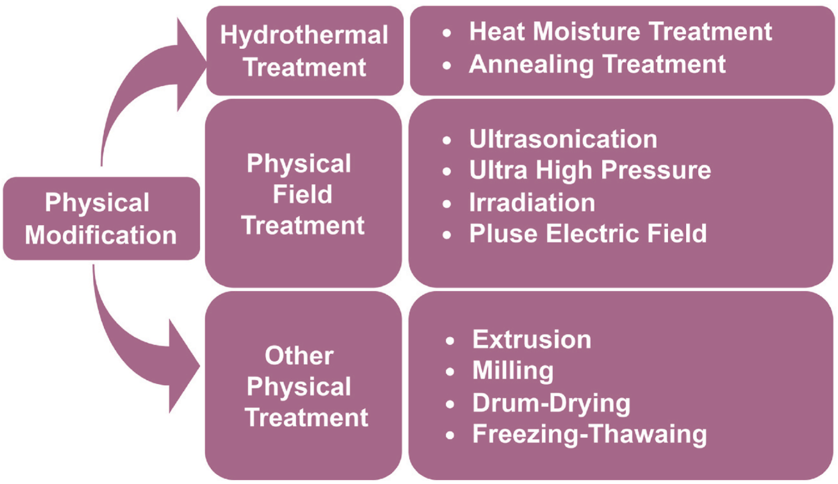

Fig. 5. Physical modification techniques for starch.

improve its physicochemical and functional properties for industrial applications [33,34].

7.1. Physical modification

Physical modification of starch refers to starch treatments using thermal-mechanical force or physical field [31]. Physical modification of starch falls typically into three categories: hydrothermal treatment, field treatment, and other physical treatments (Fig. 5). Modifications to the physical form are often "green" for the environment, risk-free for industrial production, and easy to implement in commercial settings [75,76,82].

7.1.1. Heat moisture and annealing treatment

The first modification treatment procedure in the hydrothermal section of the physical modification process is the heat moisture treatment process [82,101]. The extracted starch with deficient moisture levels is heated at a high temperature during the heat-moisture treatment (HMT) process, which typically ranges from 80 °C to 140 °C. Generally, the heating process is conducted for 15 min, which can be further prolonged for 72 h. Fonseca et al. [102] reported the influence of HMT on starch directly depends upon the heating temperature, amylose, water content, and the nature of starch. Usually, the morphology of the starch granules (shape and size) modified by employing HMT remains intact h; however, in some cases, the granules of some starches get cracked when subjected to the HMT. HMT-modified starch with sodium tripolyphosphate and sodium chloride showed less amylose leaching, greater pasting temperatures, lower pasting viscosities, and lower gelatinization enthalpies than HMT starch without salts [20,82]. The inconsistent partial gelatinization process of the starch granules during HMT is typically the cause of these morphological variations. The effect of HMT on gelatinization properties is unpredictable; for example, starch enthalpy changes might increase, decrease, or stay constant following HMT treatment. The reduction in the enthalpy during the HMT process is due to the removal of specific double helices in crystalline and amorphous starch granules. The HMT process also results in the gelatinization of the starch, during which the amylopectin molecules and unstable amylose get disorganized, eventually altering the morphological properties. The two reasons for the disorganization of the starch granules include, firstly, the disruption of the unstable starch granules leads to higher temperature requirements for breaking down the remaining starch granules and, secondly, the occurrence of crystalline perfection. Heat-moisture-treated amaranth starch exhibited thermal stability with limited swelling, a high gelatinization temperature, and an elevated pasting temperature [82,102–104].

Therefore, annealing is the second modification treatment procedure in the hydrothermal section of the physical modification process. Starch granules are subjected to heat and either an excess of water or an intermediate level of water content during the annealing process, which results in a physical transformation of the starch. Granules of starch are held throughout the annealing process for a predetermined amount of time at temperatures that are above their glass transition but significantly below their gelatinization temperature. Annealing improves heat stability and lessens the degree to which starches are set back [102,103]. Typically, the changes in the structure and valuable qualities of the starch after annealing are more pronounced at the higher annealing temperature. Several studies have shown that annealing did not alter the morphology of starch granules, whereas others demonstrated that the surface pores of starch granules became bigger and more frequent. Annealed starches have been used in canned and frozen foods and in the creation of rice noodles made from long-grain rice that has been stored for an extended time, despite that a lengthy storage time is known to reduce the swelling of starch granules with improving pasting and gelling properties of the starch [82,101–106].

7.1.2. Ultrasonic treatment

Ultra-sonication is an innovative, unique, non-thermal, and environmentally friendly processing method that may produce the physical de-polymerization of the starch. The application of ultra-sonication treatment results in a phenomenon known as acoustic cavitation, which is the rapid development and dissolution of bubbles in a liquid subjected to high heat and pressure for a short period [76,107]. High-power ultrasound was used to modify kiwi starch to determine the structure and functional properties with varying treatment powers and time. Ultrasound treatment disrupted granular morphology, produced holes on the surface, and decreased particle size and short-range molecular order of kiwi starch. The amylose concentration, swelling power, water solubility, and viscosity of the kiwi starch were increased while the gelatinization temperature decreased after high-power ultrasonic treatment. Starch's physicochemical and functional characteristics are modified using ultrasonication, which has various benefits, including improved selectivity and quality, less chemical consumption, and quick processing times [107]. As an environment-friendly method, it is used extensively in the food and biological industries to preserve and process food, emulsify, make starch inclusion complexes and edible films made from starch, and make bioethanol. The ultrasonic parameters, like energy, time, amplitude, and temperature, significantly define the effects of ultra-sonication treatment on starch's properties. Generally, the application of ultra-sonication treatment may influence morphological and structural changes. Yadav et al. [108] reported that the application of ultra-sonication during the hydration of finger millet might minimize the processing time and anti-nutrient content of finger millet with enhanced the water-binding ability and solubility of finger millet starch. Most granules remained intact after treatment at 300 W, with just a little roughened granule surface; nevertheless, as power increased, it became increasingly apparent that the granule surface had been destroyed, and irregular forms had emerged on the starch granule surface. The alterations in the starch granule morphology prominently depend upon the applied mode ultrasound mode example; continuously treated starch at 200 W had a significantly fractured granule structure, while intermittently treated starch at 400 W exhibited only minor fissures on its surface [107–109].

7.1.3. High pressure processing

High-pressure techniques are usually employed for sterilization and enzyme elimination. It is also considered an efficient and environmentally friendly method of starch modification. Majorly high-pressure homogenization (HPH) and high hydrostatic pressure (HHP) are two prominently employed methodologies in the treatment process. Applying high-pressure treatment may change and break down the non-covalent bond, creating desirable starch characteristics. Moreover, high-pressure treatment can assist in facilitating chemical alterations to enhance starch through processes like acetylation, cross-linking, and hydroxyl-propylation [109–111]. A minimal amount of research is conducted on using ultra and high-pressure treatments to modify the millet starches. An increment in the final viscosity, pasting temperature, peak time, and hold viscosity is observed when the proso millet starch is modified through UHP at altering pressures.

In contrast, the starch treated at high pressure exhibits decreasing peak and breakdown viscosity values. Ultra-high pressure treatment is also responsible for the destroyed ordered structures of native and annealed starches, resulting in a progressive gelatinization and crystallization of starch. Compared to native starch, annealing slows starch granules' internal and external structural deterioration and causes relative crystallinity to decrease as pressure rises. UHP treatment slows the gelatinization process or enhances starch's pressure resistance [109–113].

7.1.4. Irradiation treatment

Gamma radiation has a high intensity and a potent capacity to enter food since it is produced from radioactive isotopes cobalt-60 or cesium-137. In starch granules, gamma irradiation virtually resulted in noticeable morphological alterations, whereas some researchers demonstrated that the starch granule surface had fissures or holes after being subjected to irradiation treatment. The increased radiation exposure results in a reduction in the relative crystallinity of the starch. It is seen as a promising food processing technology with the potential to replace chemical and enzymatic procedures employed on a large scale for starch modification since it doesn't need the addition of chemical reagents and is simple to use without additional equipment [113–116].

7.1.5. Pulsed electric field

The pulsed electric field (PEF) has been considered a promising green technology in the food processing industry. PEF technology employs very brief bursts of strong electric fields with a field intensity of 10–80 kV/cm and a period of microseconds to milliseconds [117]. The period is intentionally kept short to prevent undesirable heat build-up and unintended electrolytic reactions. The brief electric pulse is administered to the samples by placing them between a set of electrodes, and the treatment time is then determined by multiplying the pulse length by the number of pulses. The electric field may have a variety of manifestations, including oscillatory pulses, square waves, bipolar waves, or exponentially decaying waves. The application of PEF had little to no effect on granule intactness, but some granules began to aggregate and became corrupted up to 50 kV/cm. The aggregation and surface disruption may be owing to the surface gelatinization of starch generated by PEF, which may produce high temperatures locally due to the particular electric conductivity of starch granules. It has been observed that PEF affects the pasting, thermal, and in vitro digesting characteristics of several starches up to 50 kV/cm. PEF with high electric field strength tends to lower starch breakdown viscosity and viscosity during pasting events. The thermal investigation by DSC (differential scanning calorimetry) revealed that PEF tends to reduce the enthalpy change and gelatinization temperatures and the gelatinization temperature range. The alterations caused by PEF treatment with high electric field strength (50 kV/cm) seem smaller than other physical modifications like -irradiation and high-pressure therapy [117–119].

7.1.6. Other physical treatment

Starch granules have the potential to undergo physical transformations during the processing of grain or other starchy materials. Milling is a crucial procedure for millet and cereal grains, during which the starch granules of cereal grains or starch alone are often harmed, resulting in the disruption of starch crystallites and granule shape, which in turn depends upon mechanical force magnitude and grinding time [120]. Extrusion is an essential technique to modify starch preparation for low-moisture cereal-based food. Extrusion causes gelatinization of starch granules and fragmentation of amylopectin molecules owing to high pressure, temperature, and mechanical force [121]. It has been discovered that using drum drying to prepare food alters the functional characteristics of starch, which depend on the amount of water present, the drying procedure, and the temperature. There have been reports of further treatments, including freezing-thawing and cold plasma, all of which still need research [120–122].

7.2. Chemical modification

The origin of the starch, reaction conditions, types of substituents, degree of substitution, and the arrangement of these substitutes within starch molecules collectively influence the chemical and functional alterations that occur during chemical starch modification [123,130,131,134].

7.2.1. Etherification

Products containing hydroxy-propylated starch, also known as starches altered through the etherification process with propylene oxide, have widespread use in agri foods. The procedure reduces the propensity of starch to turn into paste and degrade while simultaneously preserving the starch capacity to provide the necessary dietary functionality. The paste and gel obtained from hydroxypropylated starch showed good textural qualities, reduced syneresis, and were more resistant to freezing, thawing, and cold storage conditions. The modifications of starch, known as hydroxyl propylation, led to a decrease in the peak time and setback viscosity and an increase in the peak viscosity [124,134]. Hydrophilic linkages, which made it easier for water to penetrate the starch granules, were responsible for decreased peak time.

In contrast, higher water penetration accelerated amylose leaching and raised sample peak viscosity (PV). The gelatinization temperature and its related enthalpy was reported to decrease with increasing level of hydroxy propylation, which might be ascribed to increased structural flexibility [125]. A Differential Scanning Calorimetry examination of the starch found that after hydroxy propylation, starch degradation was significantly decreased. The explanation is that the stored starch gels had less ordered recrystallization than fresh gel t, requiring low heat to re-gelatinize the stored gels. The modified starch also had a greater capacity for free swelling, reduced turbidity, and increased paste clearness, making it helpful for creating food goods [124–127].

7.2.2. Esterification

The esterification process adds additional functional groups, which change the structure of the starch and impact the starches' functionality. The most prevalent substitution in starch modification includes octenyl, acetylation and succinylation [125–127]. These techniques produce starch with enhanced techno-functional characteristics, eventually making the starch desirable in numerous agri-food businesses. Starch granules were deformed by succinylation, but acetylation and octenyl succinylation exhibited no appreciable deformation. Esterification of starch generally improves its solubility, with the exception of acetylation, which was observed to cause amylose leaching. In addition, succinylation and octenyl succinylation enhanced the swelling characteristics of starch due to the steric barrier between the individual starch chains. They made it easier for water to percolate through the starch granules. Succinylation swelling power was more significant than octenyl succinylation due to the occurrence of water loving succinyl groups. The retrogradation enthalpies of the modified starches are found to be lower by researchers as compared to native starch due to random reassociation of α 1,4 glycosidic linkage, which did not have achieved a comparable degree of crystallinity as they had before the process.

In pearl millet starch, the gelatinization parameters decreased with increasing substitution level and reaction time when modification by esterification process [127–129]. The inclusion of hydrophobic alkenyl groups caused the hydrogen bonds to weaken, which led to a decrease in the gelatinization temperature and enthalpy. As a result, the enthalpy of esterified octenyl succinic anhydride starch is reduced, enabling starch to expand even at reduced temperature [129]. Esterification methods for starch modification might be carefully chosen based on the required functionality and potential use in the formulation of food products.

7.2.3. Oxidation

Oxidation is another method of chemical modification. It results in the replacement of hydroxyl groups with carboxyl (R–COOH) and carbonyl groups (C═O), which causes alterations in the structure of starch influencing its characteristics [130–132]. Shear stability, swelling capacity and solubility of starch were found to be improved in the oxidized starch due to considerable decrease in the breakdown viscosity, depolymerization and inclusion of the hydrophilic group respectively [132]. The oxidation of starches impacted their rigidity and tensile strength, reducing their flexibility while becoming a key component in crafting biodegradable films. These films exhibit elevated mechanical properties and an appealing visual quality. However, peroxide value was found to be increased while oxidation treatment due to the integration of COOH-R and C═O groups [68,132,133].

7.2.4. Crosslinking treatments

The cross-linking agents such as epichlorohydrin (EPI), sodium tripolyphosphate (STPP), sodium tri-meta-phosphate (STMP), and phosphoryl chloride have shown the most significant application in the food processing sector. These chemical agents influence the physical characteristics of starches, causing them to have a higher viscosity than those treated with EPI and STM. The concentration and composition of crosslinking agents, source of starch, pH, time, and temperature directly impacted the properties of starch. Cross-linked starch films produced by cross-linking pearl millet starch at three levels (1, 3, and 5 %) with sodium trimethophosphate exhibited lower moisture, solubility, water vapor permeability, and elongation at break values while exhibiting higher thickness, thermal and mechanical properties. The swelling power (SP) of the starch cross-linked with minute quantity of phosphoryl chloride was increased, which could be attributed to the incorporation of the phosphate groups into the starch molecules [17,75]. The EPI crosslinking method enhanced the crosslinking density, which reduced the amount of starch granule disintegration during the gelatinization process and decreased the solubility of the cross-linked starches.

Additionally, the crosslinking of starches boosted peak time and decreased peak, breakdown, and setback viscosity. Compared to native starches, the crosslinking of starches lowered the starch rapidly digestible starch (RDS) and slowly digestible starch (SDS) concentration and raised the RS. Therefore, the addition of higher amounts of crosslinking agents and their interaction with starch results in lower digestibility of starch due to severe inhibition of the swelling of the starch granules, which in turn inhibits the accessibility of the amylase enzyme to the starch granules [74,75]. The incorporation of crosslinking agents resulted in the observation of modifications to the granular structure of the starch. The surface of the cross-linked starches seemed to be somewhat rough, with a small number of dark zones and dents on the surface compared to the native starch. Crosslinking stabilizes the starch granules and fortifies the delicate starch by adding chemical bonds at random sites inside the starch granules. Cross-linked starches produce very viscous pastes that are less prone to break down during prolonged heating and vigorous stirring. The hydrogels prepared from kutki millet starch with the addition of amino acids (lysine (positively charged), aspartic acid (negatively charged), and threonine (neutral) at different pH levels may be used as a cross-linker to modify the starch by introducing new functional groups between the chains. It demonstrates that lysine amino acids may be a more effective cross-linker for the alteration of, on the other side, the starch of kutki millets also used for developing gelling agents to deliver nutraceuticals substance [75,76,126]. Sharma et al. [133] used barnyard millet starch to cross-link with sodium trimetaphosphate at varying concentrations (1, 3, and 5 %). The results of his study indicated that the cross-linking reduced the concentration of amylose content of native starch. The cross-linked or modified starch showed lower swelling power (SP) and solubility, lower peak, and breakdown viscosities but greater pasting temperatures than native starches. The lower water barrier properties, highest mechanical strength, and solubility were reported in cross-linked starches compared to native starch [127,128]. Crosslinking also prevents starch decomposition, reducing its digestibility; consequently, it might be used in healthy food items.

7.3. Biological modification

Modifying starches with enzymes has been extensively recognized and performed since it eliminates toxic and harmful chemicals [32]. Fragile granules of starch are destroyed by it, and as a secondary effect, it causes the granules' surface to develop many tiny holes and pores. This results in a decrease in the water-binding capacity of the starch suspensions and their viscosity. The application of enzymatic modification breaks down amylose into oligosaccharides of lower molecular weight in starches with high amylose concentration. This modification method generates highly branched amylopectin and amylose, which, when combined, create starch with improved water solubility and decreased digestibility; both characteristics are desired in the beverage industry. The modification treatment produces more amylose chains, which hinders the water absorption of the starches in finger millet and resulting in a lesser swelling power. Enzymatic modification changed starch by decreasing syneresis, and an optimum transmittance for finger and pearl millet-modified starch is also reported. Enzymatically treated pearl millet starch had nearly the same freeze-thaw stability, pasting behavior, color value, and paste clarity as acid-treated starch [17,19]. The improved starch properties might be attributed to the increased stability of starch due to more substantial intra and intermolecular interactions between starch chains. To produce the desired product consistency in food goods such as jellies and pastes, this kind of behavior is essential in such products. As for its benefits in terms of environmental concerns, the enzymatic modification approach, also known as green technology, may easily take its place compared to the other chemical modification techniques [30,32,134].

7.4. Other (dual) modification processes

Studies on the use of several modifying techniques simultaneously are currently limited for millet starches; nevertheless, their utilization may enhance the functional properties of starch [136]. Dual modifications are processes in which two modifications are simultaneously applied to achieve starches' desired physiochemical and morphological characteristics. Comparisons were made between the native and modified starches obtained from foxtail millet through the processes of ultra-sonication, annealing, and a grouping of the two treatments. These starches were then evaluated for their physiochemical and morphological properties. Starch amylose and amylopectin content were altered by sonication treatment, which changed pasting characteristics of the starch. The starch showed higher amylose content and resistant starch value than native starch, enhancing the shear stability and acidic resistance by applying ultra-sonication treatment followed by annealing application of sonication after annealing aided in cavity development and increased final viscosity [112,136–138]. A greater swelling power was seen in the ultrasonic-treated starch as compared to both the native and annealed starches, along with enhancing the breakdown and peak viscosity. The dual modification brought in a rise in the color scale value of L*, which indicated a higher level of purity. Annealing followed up by ultra-sonication exhibits an optimum enhancement in final viscosity due to the formation of cavities. The annealing of foxtail millet starch resulted in rearranging the starch chains in the crystalline and amorphous sections of the granules, which contributed to an increase in the granules' degree of stability and crystalline structure. The degree of crystallinity of starches was also shown to rise after annealing.

Regarding textural qualities, the ultrasonic treatment lowered the hardness of the starch gel, whereas annealing enhanced it. The modified starches exhibited less springiness and cohesion than the unmodified starches while least affecting the gumminess and chewiness. Ultra-sonication annealing (USA) demonstrated the most desired features among all starches, such as solid shear, acid resistance, and enhanced gel texture [135–139].

8. Effects of modification techniques on the functional properties of starch and their health benefits

The modification techniques of starches significantly influenced the physicochemical and functional properties (crystallinity, solubility, surface properties, swelling, viscosity, pasting, gelatinization, thermal, freeze-thaw stability, mechanical, gelling, etc.) of starches [140,141]. Numerous researchers have reported that modifying approaches may help improve application starch functionality [45–142]. On the other side, Ashogbon and Akintayo [123] said that the modification approaches may affect the functionality and structure of the starch molecules. For example, Javadian et al. [145] applied dual modification (Hydroxypropylation and acid hydrolysis) approaches on the tapioca starch to investigate their effects on the functional, structural, and thermal properties. Those reported that applying dual modification approaches significantly improved the solubility power but reduced the gelatinization temperature of the modified starch compared to other modified starch. The heat moisture treatment of starch makes it easy for water to access starch amorphous regions, and the remaining disassociated starch chains could solubilize into the water, which increases the solubility of starch as compared to native starches [143–145]. A significant change in the proso millet starch properties, such as digestive, physicochemical, and structural properties, was observed when it was subjected to the modification treatment processes like cold plasma, ultra-high pressure, or their combination. The morphological properties of the granules of proso millet starch remain unaltered for modification treatments with ultra-high pressure and cold plasma at low pressures. However, a complete gelatinization of proso millet starch is observed when the ultra-high pressure modification treatment is executed at 600 MPa, followed by cold plasma. The crystalline region of proso millet starch is partially destroyed when ultra-high-pressure treatment is performed at high pressure, followed by cold plasma [140]. According to Ashogbon [144], wheat starch modified by ultrasonication treatment shows an increase in relative crystallinity. The amorphous parts of wheat starch in the granule are more responsive to the ultrasonication treatment than the crystalline areas of the granule. An improved crystalline structure results from the reorganization of fragmented chains caused by cleavage in amylose-rich amorphous regions [137,144]. Therefore, the modified starches are also more beneficial for health benefits. Babu [138], reported that heat-treated foxtail millet starch has a hypoglycaemic effect in mice and influences gut microbiota and serum metabolic profile, which aids in controlling insulin and blood glucose levels. There are several industrial applications of modified starch in edible films, development of nanoparticles, and pharmaceutical and medical applications [145].

9. Applications and limitations of native and modified millet starch

Starch is a versatile biomaterial used worldwide for its various commercial applications in food, textile, nanotechnology,

Table 6
Applications and limitations of native and modified millet starches.

Starch sources	Modification Treatment	Key findings	Industrial application	References
Proso	AMT	Reduced the amylose content and WBC of starch, and also improved the clarity of the starch-based paste	Noodles, canned and frozen foods	[169]
	HTM	Increased the amylose content in starch, and WBC and reduced the paste clarity		
Kutki	AMT	Improved swelling, viscosity, and structural integrity of the gel.	Fat replacer	[17]
	NS	Higher amylose and showed better pasting, textural properties	Thickener, stabilizer, and gelling agent	
Finger	Oxidized and acetylated	Decrease in disintegration time and friability, however, increase in crushing and tensile strength (starch compacts)	Capsule and Tablet formation	[165]
	NS	Excellent functional properties such as solubility, swelling index, and water vapor permeability,	Thin and flexible food packaging film.	[156]
	UAH	Improved structural morphology, WBC, and solubility	Food products	[108]
Teff	NS	Improved radical scavenging activity and mechanical properties	Antioxidant packaging material	[170]
	Pregelatinized	Faster disintegration time and better compressibility	chloroquine phosphate tablets	[171]
Foxtail	AUS, USA	Improve starch stability and gel formation	Food products	[138]
	NS	More opacity, uniform 3-D cellular structure + hexagonal structure	Starch gel	[172]
	NS	Improved packaging material (antimicrobial, antioxidant activities)	Cheese Packaging	[173]
Barnyard	Cross-linking	Higher tensile strength, barrier and mechanical properties	Starch-based films	[135]
	NS	Improved antioxidant, decreased solubility and WVP	Starch film containing borage oil	[174]
Pearl	HP	Improved consistency, graininess, taste, and overall acceptability	White sauces	[175]
	SUS,OXS,ACS	Improved cold storage stability	custards	[176]
	HMT, MT, ST	Increased amylose content, transition temperatures and swelling capacity	Film formation	[70]
	HP, succinylated, oxidized, and acetylated	Improved cold storage stability, textural and sensorial properties and Reduced syneresis	Custards	[166]
	Octenyl Succinic Anhydride	Improved pasting viscosity, water solubility	Biodegradable starch films	[125]
	Cross-linked	Lower moisture, solubility, water vapor permeability (WVP),	Film Loaded with Fenugreek Oil	[74]
Kodo	NS	Lower WBC, swelling power, viscosity, and dispersibility, higher fat absorption capacity and solubility percentage	–	[167,168]

Where; NS (Native starch) AMT (Acid Modification) HTM (Hydrothermal), UAHT (Ultrasound-assisted hydration), Annealing and ultra-sonication (AUS) Or ultra-sonication and annealing (UAS), HMT (Heat moisture treatment))MT(Microwave treatment) ST(Sonication treatment), HP (Hydroxy propylated), WVP (water vapor permeability), TPC(Total phenol content), WBC(water binding capacity) succinylated starch (SUS), oxidized starch (OXS) and acetylated starch (ACS).

pharmaceutical, and engineering industries. Starch's physicochemical and functional qualities determine whether it will play the role or perform the functionality sought in a particular field [15–27]. Remarkably, the starch produced from millet is widely used in the food processing sector as native and modified starch. Millet starch has limited functionality and, consequently, few industrial uses. Both native and modified starches serve various purposes: they function as binders and thickeners in baked goods and meat products, act as fat replacements in ice creams, encapsulate flavours, stabilize emulsions in juices and beverages, serve as gelling agents in gums and gels, stabilize foam in marshmallows, and function as crisping agents in fried snack items [14,17]. The modified (pre-gelatinized, acetylated, acid-modified, and esterified) starch is also used in the pharmaceutical sector to manufacture capsules as a carrier of drug delivery agents. The previous applications of modification methods on the properties of the millet starch and their industrial applications are summarized in Table 6. The limitations of millet starch in food formulations have not been reported as such as yet. Conversely, the millets also provide a challenge in their processing because of their small grain size [16].

Additionally, a significant quantity of modified millet starches is high in amylose, inhibiting the functionality of several constituent parts. Millets have less swelling power than traditional starches like wheat and rice, which may limit their applications. The resistant starch content of millet starch varies, with low RS content millets being advantageous for easily digestible food formulations, including those for infants and convalescents, and high resistant starch content millets with greater paste viscosities and low ability to retrograde being suitable for a variety of food applications, similar to waxy corn starch [17,28].

10. Conclusions

Millets are highly nutritious and contain valuable functional components, including starch. Millet starch has numerous industrial applications as a structural agent, binding agent, texture modifier, and viscosity regulator. Compared to other starches, millet starches are slowly digestible and good for the people suffering from diabetes. However, its utility is limited because millets cannot be produced in large quantities and are grown only in a few specific regions worldwide. The extraction of millet starch typically involves wet milling techniques using water, alkaline, or acidic mediums. Among these methods, the alkaline process is generally considered most effective for obtaining a higher yield of millet starch since it solubilizes the protein component and extracts starch more efficiently. The several physical, chemical, and biological methods of the starch modification have been reported in which, ultrasonication method is considered environmental friendly and safe method for modification and extraction of high quality starch for industrial applications. The future research should be explored to compare the effects of different physical, chemical, biological and hurdle methods on the functional and structural properties of millet starch for wide applications.

CRediT author statement

Heena and Nishant Kumar: Formal analysis, Data curation, Conceptualization, Writing original draft, Writing – review & editing. Rakhi Singh: Conceptualization, Validation, Supervision, Project administration, Writing – review & editing. Balendu Shekher Giri: Writing – review & editing, Validation. Ashutosh Upadhyay: Supervision, Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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