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Review

Ball-milling: A sustainable and green approach for starch modification

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ABSTRACT

Ball-milling is a low-cost and green technology that offers mechanical actions (shear, friction, collision, and impact) to modify and reduce starch to nanoscale size. It is one of the physical modification techniques used to reduce the relative crystallinity and improve the digestibility of starch to their better utility. Ball-milling alters surface morphology, improving the overall surface area and texture of starch granules. This approach also can improve functional properties, including swelling, solubility, and water solubility, with increased energy supplied. Further, the increased surface area of starch particles and subsequent increase in active sites enhance chemical reactions and alteration in structural transformations and physical and chemical properties. This review is about current information on the impact of ball-milling on the compositions, fine structures, morphological, thermal, and rheological characteristics of starch granules. Furthermore, ball-milling is an efficient approach for the development of high-quality starches for applications in the food and non-food industries. There is also an attempt to compare ball-milled starches from various botanical sources.

1. Introduction

Generally, milling refers to a mechanical operation employed for the size reduction of solid materials with consequential changes in properties. Grain milling pertains to the comminution of the seeds of maize, rice, wheat, barley, and other coarse grain crops. It can also be explained as converting raw materials into a primary product for secondary processing. During grain milling, grains such as corn, rice, wheat, and oats are de-husked and ground into smaller pieces or flours to enhance palatability, reduce cooking time and create food products. Various mills are used to grind grains and refine processes, including stone, disc, roller, hammer, and ultra-fine [1]. Stone and hammer mills are usually single-pass systems, whereas roller mills are multi-pass systems with corrugated break rolls and reduction rolls. The stone mill crushes the kernel between two stones and grounds them finely as they reach the periphery of the stones. Hammer mills use impact and fracture through fast-rotating hammers to break the kernels [2].

Milling and refining cereals (maize, wheat, corn), and tubers (potato and cassava), lead to starch production. Starch granules damage during milling operation due to various shear and compressive forces acting upon them, altering their morphology and functional properties, viz. solubility, swelling power (SP), heat-stability, retrogradation, pasting behavior, and digestibility [3].

The ball-milling is gaining attention as it is capable of fine-grinding grains and ensures higher safety, simplicity, cost-efficiency, and lower effluent generation containing salts or reagents and their by-products compared to other non-thermal treatments [4,5]. It refers to applying friction, shear, collision, impingement, and various other forces to modify the microscopic structure of solid particles [6,7]. Ball milling alters granular morphology, molecular weight, crystallinity, and amylose/amylopectin ratio of different starches [8–11]. Reduced size, increased surface, and increased active sites of starch molecules enhance the occurrence of chemical reactions and alteration in physical and chemical properties [12]. Ball-milling modified starches could be used for various applications, as emulsifying agents, fat replacers, and wall materials to encapsulate desired compounds, among other applications as modified ingredients in pasta, noodles, and dumplings [13,14].

2. Mechanism behind ball-milling

During ball milling, solids constantly undergo stress, aggregation, and agglomeration, which allows the material to interact and experience various chemical reactions under mechanical forces [15]. In a high-energy mill, the material to be milled is placed in a hollow cylindrical

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container and a milling medium, i.e., balls generally made of stainless steel, ceramic, or rubber. The container rotates in a particular direction, causing the balls to rotate in the opposite direction, leading to alternative synchronization of centrifugal forces. The milling balls roll on the inner side of the grinding jar, resulting in frictional forces on the material. The striking of the balls on the opposite wall of the container produces a high impact force on the material. Due to the motion of balls, the kinetic energy produced acts upon the material, sufficient to break down chemical bonds of molecules and to cause a reduction in particle size. Successive mass and energy transfer occur in the process, and mechanical stress generated in the operation breaks down the lattice structure of the material. The operating parameters of the ball mill need to be optimized in terms of speed, grinding time, ball-to-powder ratio, milling load, milling energy, humectants, etc., to achieve the required size reduction without damaging the particles [16]. The friction between starch granules produces heat to modify its properties [17].

Ball milling of solid particles through mechanical force shows different combination of impact, shear, and friction forces (Fig. 1a). During the initial stage, the impact force from the balls on the particles flattens them out due to compressive forces. Following this, it reaches an intermediate stage, where the mixture is broken down to a micrometer scale. Still, the mass obtained is not homogenous, whereas in the final stage, further comminution becomes more evident physically, and homogenous mass is achieved at the microscopic level. The completion stage is the last stage in which no further physical improvement in the dispersion can be achieved. The particles become highly deformed with metastable structures, and lamellae can no longer be observed under optical microscopy. The physical agitation caused by the balls during ball milling caused the macro starch granules to fragment, which decreased the average size of the starches. The source of the starch, starch composition, and amylopectin branching primarily governs this fragmentation and size reduction of particles [18].

3. Types of ball mills and their influencing factors

Ball-mills are categorized into four types depending on the motion generated to produce momentum in grinding balls and act upon the material with various milling forces. These are planetary, tumbling, vibratory, and attrition mills.

3.1. Planetary ball mill

Planetary ball mills are simple and efficient in producing ground/pulverized material. The mill usually contains two or more jars mounted on a sun wheel rotating at a particular angular velocity and rotating at their axis with a specific angular velocity [19]. The jars are Teflon or stainless steel and are hermetically sealed [17]. The grinding jar and the sun wheel rotate in the opposite direction, due to which the milling balls are subjected to superimposed rotational motion. The combined action of two centrifugal fields causes a non-uniform acceleration within the chamber [20]. The kinetic energy of milling balls is about 100 times that of gravitational force due to coriolis and centrifugal forces generation. Milling speed, grinding time, and ball-to-powder ratio affect the particle size obtained and morphology of the solid particles [5].

3.2. Tumbler ball-mill

Tumbler ball mill utilizes gravitational force to exert force on the solid particles. The milling balls rotate axially due to friction against the wall, and it rolls down and impacts against the material. The particles encounter multiple collisions with impact forces and attrition forces as they get caught between balls and balls and the walls of the container. The effectiveness of the tumbler-type mill depends on the mill chamber diameter. The larger the mill diameter, the greater is fall height for the ball. Hence, increased energy transmission to the balls occurs. Also, the rotational speed of the vessel needs to be optimized where the gravitational force is in equilibrium with the gravitational force. If the rotational speed exceeds this limit, the centrifugal force surpasses the gravitational force, and balls will keep rotating in the inner periphery of the chamber [16,21]. The common type of tumbling ball mill used is the bond ball mill. The small-scale mill is 30 cm in diameter and 30 cm in length. Generally, <300 balls of 40 mm size can be used. Small-sized mills can be operated at 20 % mill filling and 50 % powder filling [22].

3.3. Vibratory mills

In vibratory mills, the cylindrical vessel and milling balls are oscillated at very high frequencies and low amplitude. The efficiency of a vibratory mill depends on the vibration amplitude and mass of the milling medium [16]. Vibrations amplify the shock-erasing effect due to variations in strength and frictional components responsible for fine

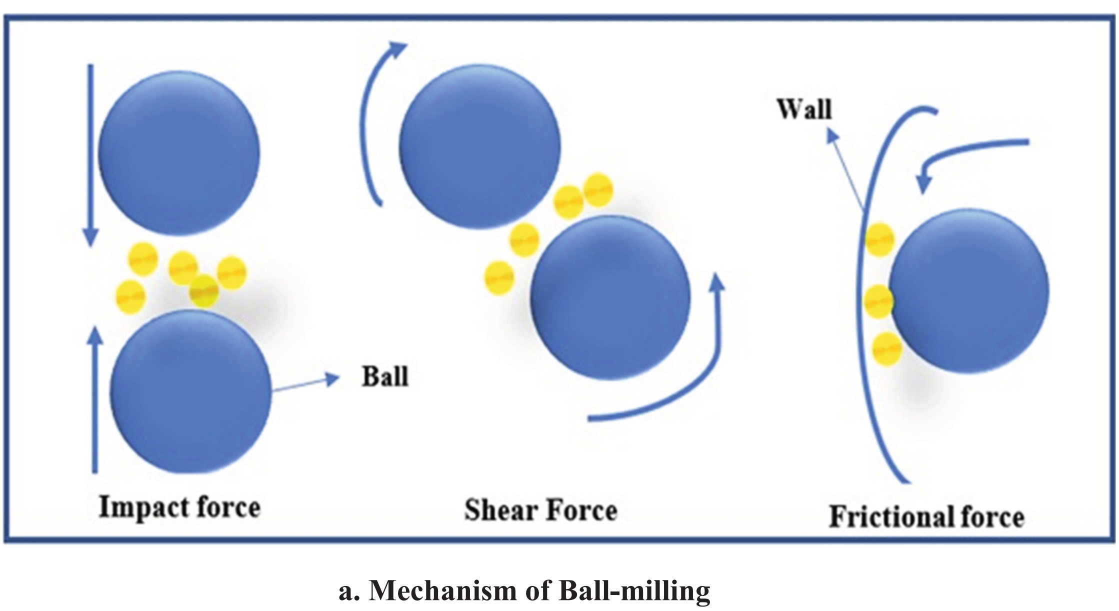


Fig. 1a. Mechanism of ball-milling.

grinding. The rate of destruction increases under cyclic loads and increased dynamic interactions between particles. The energy from the electric motor is transmitted to the driving shaft as rotational torque. The unbalanced masses on the shaft ensure the generation of combined force and moment imbalance to the central axis of grinding chambers [1]. Generally, 20-30 mm of the trajectory of milling balls can be achieved with a vibratory amplitude of 20 mm. The force impinged by balls upon the material under vibration is significantly higher than planetary mills [21].

3.4. Attrition mill

A vertical rotating shaft is mounted onto a stationary vertical cylindrical vessel in an attrition mill. The rotating shaft is further connected to multiple horizontal arms. The balls and solid particles/material tumble randomly due to high-speed rotating arms. This action produces impact forces along with shear and frictional forces due to collision between balls, vessel wall and balls, and balls and impellers. Attrition mills have significantly lower specific power consumption than planetary/vibratory mills, as the energy is directly utilized to rotate milling balls and is not required to vibrate the whole chamber/vessel. The only fallback of using this type of mill is excessive wear on the mill bodies during the process, which may also cause contamination of the material. The size, the number of balls, milling speed, and temperature are major factors determining the efficiency of the attrition mill [21].

3.4.1. Milling time

An increase in milling time results in bigger particle sizes with irregular shapes, an unsmooth surface, and particle agglomeration compared to native starches [23]. The agglomeration could be due to the breakdown of starch granules into smaller fragments that lump together to the surface of the larger granules by H-bonding, van der Waal, and electrostatic interaction, and high surface area [24]. Increasing the milling time up to a specific time interval increased the span and particle diameter of the ball-milled starches, and milling beyond this time decreased the span and particle diameter of the overall fraction size. It must be noted that span is the length of time in which the fractional particles remain in the same state (altered or unaltered). The bulk material (starch) is fragmented during the ball milling process; fractions of particles are obtained; their sizes are defined as the fraction sizes.

3.4.2. Milling load and milling energy

The particle size of ball-milled starch differed with the milling load and energy. When the milling load is decreased, the D (4,3) values of milled starch increased, while at higher milling loads, the particles of 15–40 mm decreased, and those in the range of 0–15 mm increased. Loading of starch also affects the milling process, and at a high load, the milling balls rub the starch surface, and this function gradually turns to flatten as the milling load decreases [25]. This simply means that at high loading, the balls have easy access to the surface of the starch granules, and this function decreases as the milling load decreases.

An increase in the milling energy results in a decrease and disappearance of the residual fraction of starch particles with a larger size and decreases the particle size due to high-impact milling [26]. An increase in milling energy also decreases the specific surface area, attributed to reduced dynamic equilibrium between large particles crushing into smaller particles and their accumulation. High-impact milling generates great surface energies, favoring agglomeration [26].

3.4.3. Humectants

The humectants used in wet ball-milling of starches play a significant role in altering the particle size and distribution [27]. The water hydration and starch are important for granule agglomeration besides van der Waal's and electrostatic force. Ethanol as humectants instead of water reduces gelatinization, which happens during the milling in a liquid environment. Furthermore, Diop et al. [18] showed that in wet ball-milling of starch with ethanol, the particle size increases compared to dry ball-milled starch. At a higher starch concentration in comparison to ethanol, the wet sediment becomes compact, which absorbs the energy from ball collisions which, result in no change in the granule size; however, at higher ethanol and lower starch concentration, the starch particles disperse more in a liquid which enhances starch granules mobility led to a better particles exposition to the ball's action [91]. A longer period of the wet ball-milling process shifted the major peak position to a smaller particle size, reduced the major peak intensity, and increased the size of the secondary peak [27].

4. Impact of ball-milling on the starch properties

Ball-milling treatments induce starch depolymerization, increase solubility, water absorption, and SP, and reduce crystallinity [5]. Several studies illustrated the effect of ball-milling treatment under varied operating parameters for altering starch granules in different applications (Table 1 and Fig. 1b).

4.1. Particle size

Different ball-milling techniques significantly influence particle size, distribution, span index, and surface area (Table 2). During ball-milling, the physical agitation by balls did the fragmentation of macro starch granules, primarily controlled by the origin, starch composition, and amylopectin branching [43]. Native starches showed bimodal particle size distribution, and ball-milled starches, in contrast, showed monomodal size distributions [26].

4.2. Starch composition

The starches with higher amylopectin content showed a greater reduction in molecular granule size after the ball-milling due to the variations in the amylopectin branching pattern and morphological differences. The planetary ball-milling treatment makes waxy starch granules easier to damage because of the re-aggregation of small fragments of waxy starches [38]. Further, Tan et al. [10] showed that D (0.5) values of the waxy corn starch after ball-milling treatment were reduced to a greater extent, while normal corn starch showed a smaller decrease.

4.3. Amylose content

The ball-milling increases amylose content, which is proportional to milling time. An increase in amylose content by ball-milling may be due to the debranching of amylopectin at α-1,6 branching points and the subsequent release of amylose molecules [42]. This depicts that the ball-milling could be desirably used to adjust the amylopectin to amylose ratio in starch and thereby modulate its techno-functional properties for applications in different food systems. Huang et al. [41,44] found that as milling time was increased, the amylose content of ground maize and cassava starches also increased as a result of the amylopectin's glycosidic connections degrading, most likely at the branch point, releasing the amylopectin's long branch chains, which were recorded as amylose. Furthermore, the increase in amylose content was reported to be larger in cassava starch than in maize starch which could be due to the fragile nature of the cassava starch granules. Jhan et al. [43] also reported similar findings for finger millet starch and sorghum starch because the physical shear forces during milling easily break the branching amylopectin, turning it into smaller linear amylose units.

4.4. Molecular structure

The intricate starch structure is facilitated by sequential confirmation and formation. This involves the arrangement of amylose, and amylopectin, the sequence of the chains linking them, and how the milling impacts them to produce milling-damaged starch (MDS). The

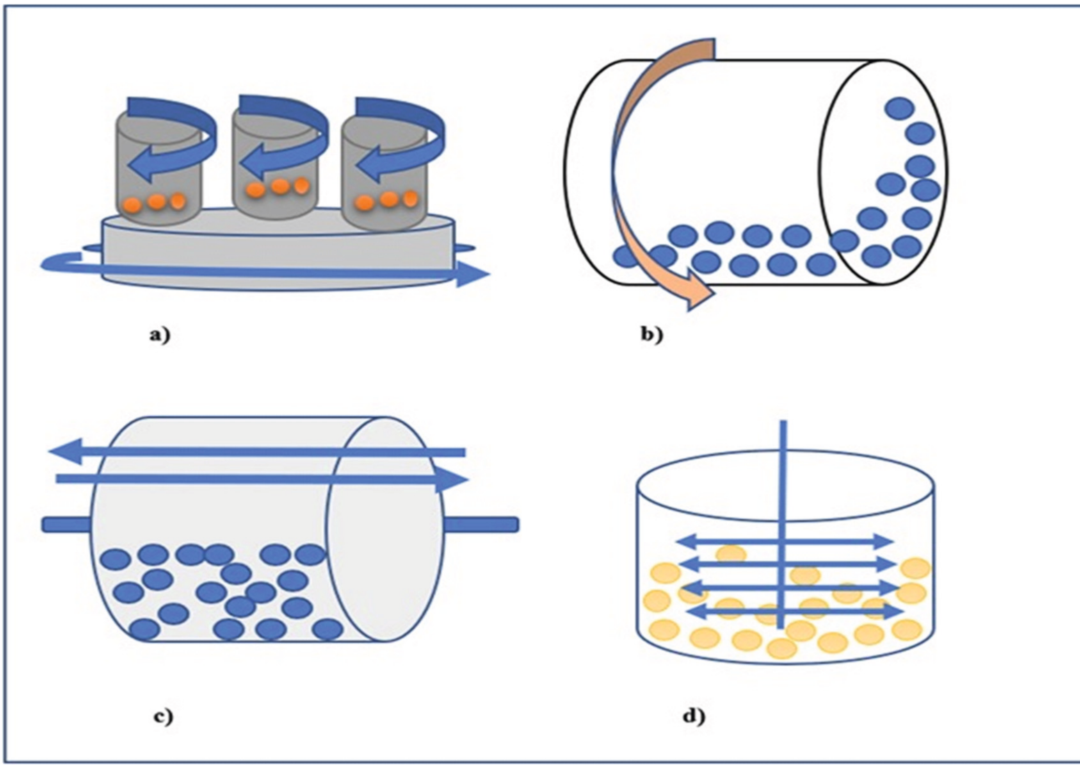
Table 1
Effect of ball-milling processing on starch granules.

Target material	Type of mill/ball-milling treatment	Operating parameters	Observations	Reference
Tapioca starch	Wet media milling	Temp-300C Speed-3000 rpm Time-0-420 min Balls mass-740 g Balls Diameter-0.5 mm Balls material-yttria-stabilized tetragonal zirconia	• Reduction of particle size to 140 nm. • Increased dispersion stability and specific surface area.	Li et al. [28,29]
Potato starch	Planetary ball-mill	Vessel capacity-80 ml Milling speed-600 rpm Balls-15 Balls Diameter-1 cm Balls material-Silicon nitrode, stainless steel, tungsten carbide Milling balls: 1:12 Milling time-5 min Sample temp-400 °C Energy supplied-0.5-4.4 J/g	• Loss in crystallinity • Coldwater solubility increased to 54 % (@ 2.2 J/g). • Swelling increased to 19 g/g (@2.2 J/g).	Juarez-Arellano et al. [5]
Water chestnut (WNS) Lotus stem (LNS) Horse chestnut (HNS)	Planetary ball-mill	Rotational Speed-600 rpm Milling time-5 h Balls-5 Balls material-Zirconium Ball size-8 mm	• Particle Size-WNS-271 nm, LNS-855 nm, HNS-343 nm • Increased water absorption activity and a decreased oil absorption	Ahmad et al. [30]
Cassava starch-ferulic acid complex	Rolling type ball-mill	Vessel capacity-300 ml Ball material-Zirconia Milling-speed-380 rpm Milling time-20, 60, and 100 min. Temperature-500 °C	• Reduced crystalline structure • Decreased thermal stability • Increased solubility of CS-FA complex	Fang et al. [31]
Asparagus leaf by-product	Ball-mill with chilled water circulation	Vessel capacity-400 ml Ball diameter-5 mm Ball material-Zirconium Material to ball ratio-1:5 Temperature-20 °C Milling time-1,2,4,6 h	• Decreased particle size to 7.5 µm • Increased water solubility • Enhanced green color with increased chlorophyll content • Increased phenolic and flavonoid content and antioxidant activity. • Increased soluble fiber	Chitrakar et al. [12]
Turmeric residue (*Curcuma Longa*)	Ball-milling	Frequency-5 Hz Milling time-24 h	• Particle size reduction to D80Value-0.265 mm	Maniglia and Tapia-Blácido [32]
Wheat gluten and olive pomace powder	Planetary Ball-mill	Vessel capacity-250 ml Ball Dia-10 mm Ball material-Zirconia Powder to ball ratio-1:10 Milling speed-150 rpm Milling time-10 h	• Improved mechanical properties of biocomposite with low filler content (15 %) • Improved mechanical and physical properties of olive pomace	Boudria et al. [33]
Potato starch	Rolling-type ball-mill	Diameter of the cylinder-9 cm Rotational speed-90 rpm Milling time-0-90 h Room temperature Ball Dia-1 cm Ball material-Stainless Steel Ball mass-384 g	• Fully amorphous starch after 17 h of milling • Increased low molecular weight amylopectin • Improved water hydration with increased processing time	Anzai et al. [34]

sequence possessed five hierarchical structural levels depicted in Fig. 2 [45]. Before ball milling, the structures of the various starches differ in their native form. Generally, the tuber starches (e.g. cassava and potato) are less resistant to ball milling actions when compared to the cereal starches (e.g. rice, corn and wheat) and legume starches (cowpea, lentil, and navy bean) due to their large starch granules and vulnerability to swelling. In contrast, the legumes are resistant to the action of ball milling processes due to their unusually high amylose content and resistant to swelling.

The ball-milling of maize starch with adding little water resulted in the conversion of some hydroxyl groups into carboxyl (0.027 %) and carbonyl (0.044 %) groups [40]. These quantitative values of carbonyl and carboxyl groups were about the same as when 0.8gCl/100 g maize starch at 35 °C for 50 min was oxidized by hypochlorite [46]. The slight oxidation during the milling was caused by free water from the added water that traps oxygen from the air [40]. By disparity, starches ball-milled in the dry state were proven by solid-state ^{13}C NMR and FTIR to have produced no carbonyl and carboxyl functional groups [36]. The added water in the previous work was responsible for the mild oxidation that created the functional groups.

In the work of Yu et al. [47], the intrinsic viscosities of the native and ball-milled starch (BMS) were 141.9 and 137.8 mL/g, respectively. In another work, 70 % amylopectin maize starch subjected to ball-milling was shown to possess an average molecular weight of 1.48×10^7 g/mol, and that of the untreated starch was 1.55×10^7 g/mol [40]. These two facts indicate a small decrease of 4.7 % in the molecular weight of the BMS and point in the direction of starch degradation due to ball-milling. The main reason the maize starch was subjected to mechanical actions of ball-milling was richly amylopectin; the degradation, de-polymerization, and de-crystallization that occurred to the starch



b. Ball-mills a) Planetary b) Tumbling c) Vibratory and d) Attrition Ball-mills

Fig. 1b. Ball-mills a) planetary b) tumbling c) vibratory and d) attrition Ball-mills.

molecules were ascribed to the breakage of the branched points of amylopectin in the starch granule. The consequence of the breakage of the branched AP chains amounted to an increase in the linear content of the amylose. This was proven by the increased amylose content from 25.2 wt% in the unmodified starch to 25.6 wt% in the BMS using a calorimetric iodine analyzer [40]. Obviously, the increased amylose content decreased amylopectin by 0.4 % due to the milling process. These small differences in the amylopectin of the native starch (NS) and BMS impacted variations in their physicochemical and functional properties.

The advantage of the added water during the milling process must be stressed because it resulted in the degradation of 0.4 % of amylopectin instead of 11.07 % in the dry milling process [44]. It means the added water aids in protecting and preserving some of the starch granules from degradation during the milling. The energies generated by mechanical and thermal agitation must have been scattered by the added water somehow uniformly, thereby minimizing the effect on the starch granules compared to the dry milling process. The added water could presumably scatter the generated thermal energy via some unit operations (absorption and diffusion) during the milling. The plasticization effect of water [48] could diminish overheating and preserve the starch granules.

5. Functional properties

5.1. Swelling power (SP)

The ball-milled starches depict higher swelling due to increased water absorption by opening up structural elements of starch. Juarez-Arellano et al. [5] observed that the cold-water swelling of ball-milled potato starch by supplying 2.2 J/g energy increased to 19 g/g compared to native potato starches with no swelling. However, the potato starches ball-milled above 4.4 J/g energy showed a decline in solubility. The increased swelling of starch molecules on ball milling is due to the fragmentation of starch molecules and the increase in their surface area. Further, the swelling is also facilitated by the expansion of amorphous rings in the inner portion of starch and the formation of H-bonds with water due to the reduction in the crystalline area. However, the ball-milling at higher energy (>4.4 J/g) causes a complete loss of starch's granular structure. Limpongsa & Jaipakdee [39] reported an increase in the swelling capacity of the ball-milled Thai rice starch, which could be due to the easy passage of water molecules into the damaged and fragmented interior portion of starch facilitated by the lack of rigid network structures and increase in free OH groups.

The ball-milling causes a damaged and porous matrix structure that facilitates water holding through hydrogen bonds, resulting in increased swelling. Further, it is observed that the ball-milling progressively converts semi-crystalline granules into an amorphous state, as evidenced by loss of birefringence and reduction in XRD peaks. It is also reported that the ball-milling reduces the double helix content in amylopectin [49], leading to increased swelling of ball-milled starches. Therefore, the ball-milling process could improve the water absorption and swelling of native starches. These ball-milled modified starches would find extensive applications in developing viscous and gel-like structures in food systems.

5.2. Solubility

The ball-milling increases starch solubility due to depolymerization. The Thai rice starch was subjected to ball-milling using 30 mm diameter zirconium oxide balls at 450 rpm for 45 min and a pause interval of 40 min after every 5 min of milling. The ball-milled rice starch improved water solubility with an increase in cold water solubility by about 5.6 times over the control sample [39].

Similarly, the cassava starch showed increased solubility from 0.48 to 93.76 % on ball-milling for 2 h; however, milling beyond 2 h has a minor effect on the solubility [44]. The cold-water solubility of potato

Table 2
Effect of ball-milling type and time on the Particle size and distribution of starches.

Starch	Ball-milling type	Average granule size (μm)	Span	Average hydrodynamic particle size	Surface area average particle size (μm)/specific area (m^2/g)	References
Maize starch	Native	D(v,0.1)-7.7 D(v,0.5)-16.1 D(v,0.9)-32.1	1.5			He et al. [35]
	Planetary ball-mill					
	Ceramic pot	D(v,0.1)-10.7 D(v,0.5)-42.5 D(v,0.9)-135.5	2.9			
	Stainless steel pot	D(v,0.1)-17.2 D(v,0.5)-58.3 D(v,0.9)-240.2	3.8			
Maize starch	Native	D(v,0.1)-6.13 D(v,0.5)-13.81 D(v,0.9)-20.13	1.01			Liu et al. [36]
	Planetary ball-mill					
	1 h	D(v,0.1)-9.15 D(v,0.5)-18.86 D(v,0.9)-31.19	1.17			
	2 h	D(v,0.1)-8.58 D(v,0.5)-19.38 D(v,0.9)-36.74	1.42			
	3 h	D(v,0.1)-7.58 D(v,0.5)-19.23 D(v,0.9)-34.70	1.41			
Josengheugchal colored rice starch	Native	D(v,0.1)-4.24 D(v,0.5)-18.98 D(v,0.9)-54.53 D_{mean}-24.51				Kim & Kim [37]
	Ball-milled	D(v,0.1)-2.71 D(v,0.5)-8.79 D(v,0.9)-49.18 D_{mean}-17.90				
Hongjinju colored rice starch	Native	D(v,0.1)-4.49 D(v,0.5)-0.74 D(v,0.9)-44.20 D_{mean}-17.90				Kim & Kim [37]
	Ball-milled	D(v,0.1)-2.48 D(v,0.5)-9.33 D(v,0.9)-34.79 D_{mean}-15.30				
Waxy maize starch	Native	d(0.5)μm-23.66				Tan et al. [10]
	Planetary ball-mill					
	4 h	d(0.5)μm-7.84				
	8 h	d(0.5)μm-6.27				
	15 h	d(0.5)μm-4.66				
	20 h	d(0.5)μm-4.61				
High-amylose corn starch	Native	d(0.5)μm-12.51				Tan et al. [10]
	Planetary ball-mill					
	4 h	d(0.5)μm-8.51				
	8 h	d(0.5)μm-8.39				
	15 h	d(0.5)μm-8.38				
	20 h	d(0.5)μm-8.36				
Pearl millet starch	Native	D(v,10)nm-1215 D(v,50)nm-1798 D(v,90)nm-2022		1972 nm		Jhan et al. [38]
	HS ball-mill	D(v,10)nm-442 D(v,50)nm-595 D(v,90)nm-803		636 nm		
Proso millet starch	Native	D(v,10)nm-1114 D(v,50)nm-1317 D(v,90)nm-1556		1456 nm		Jhan et al. [38]
	HS ball-mill	D(v,10)nm-305 D(v,50)nm-413 D(v,90)nm-533		417 nm		
Thai rice starch	Native	D(v,0.1)μm-3.90 D(v,0.5)μm-6.10 D(v,0.9)μm-9.94	0.991			Limpongsa and Jaipakdee [39]
	Planetary ball-mill	D(v,0.1)μm-23.21 D(v,0.5)μm-73.47 D(v,0.9)μm-150.30	1.730			
Thai glutinous rice starch	Native	D(v,0.5)μm-4.71	1.45			Soe et al. [23]
	Planetary ball-mill					
	5 min	D(v,0.5)μm-11.40	1.44			

(continued on next page)

Table 2 (*continued*)

Starch	Ball-milling type	Average granule size (μm)	Span	Average hydrodynamic particle size	Surface area average particle size (μm)/specific area (m^2/g)	References
	15 min	D(v,0.5)μm-14.22	1.58			
	30 min	D(v,0.5)μm-15.16	2.18			
	45 min	D(v,0.5)μm-21.00	2.09			
Water chestnut starch	Native	–				Ahmad et al.[30]
	Planetary ball-mill	D(v,50)nm-271.5				
Horse chestnut starch	Native	–				Ahmad et al. [30]
	Planetary ball-mill	D(v,50)nm-343				
Lotus stem starch	Native	–				Ahmad et al. [30]
	Planetary ball-mill	D(v,50)nm-855				
Maize starch	Native	D(v,10)μm-3.86 D(v,50)μm-16.20 D(v,90)μm-45.02	2.57			Shi et al.[40]
	Cyclotron ball-mill	D(v,10)μm-7.65 D(v,50)μm-24.91 D(v,90)μm-55.92	1.94			
Cassava starch	Native	Median (D)μm-15.99				Huang et al.[41]
	Stirring ball-mill					
	0.5 h	Median (D)μm-22.78				
	1.0 h	Median (D)μm-28.73				
	2.0 h	Median (D)μm-27.39				
	3.0 h	Median (D)μm-28.46				
Corn starch	Native	Mean (D)μm-14.06				Zhang et al.[25]
	Ball-milled					
	15 g	Mean (D)μm-15.45				
	20 g	Mean (D)μm-14.28				
	25 g	Mean (D)μm-13.76				
	30 g	Mean (D)μm-13.9				
Rice starch	Native	D_{50}μm-60.09	3.9		0.29m^2/g	González et al. [26]
	Planetary ball-mill					
	0.26 kJ/g	D_{50}μm-16.9	4.0		0.62m^2/g	
	0.52 kJ/g	D_{50}μm-15.5	3.1		0.58m^2/g	
	1.04 kJ/g	D_{50}μm-13.4	2.5		0.56m^2/g	
	1.5 kJ/g	D_{50}μm-12.4	2.3		0.57m^2/g	
	1.99 kJ/g	D_{50}μm-12.2	2.0		0.57m^2/g	
	2.36kj/g	D_{50}μm-12.8	2.0		0.55m^2/g	
	3.56 kJ/g	D_{50}μm-12.9	1.8		0.54m^2/g	
	3.56 kJ/g	D_{50}μm-13.2	1.9		0.53m^2/g	
Indica rice starch	Native	D(v,0.1)μm-1.09 D(v,0.5)μm-6.74 D(v,0.9)μm-12.42			2.58 μm	Zhang et al.[27]
	High-energy wet ball-mill					
	15 min	D(v,0.1)μm-2.17 D(v,0.5)μm-5.50 D(v,0.9)μm-10.97			4.22 μm	
	30 min	D(v,0.1)μm-1.82 D(v,0.5)μm-4.59 D(v,0.9)μm-10.60			3.62 μm	
	60 min	D(v,0.1)μm-0.36 D(v,0.5)μm-2.97 D(v,0.9)μm-6.51			1.21 μm	
	90 min	D(v,0.1)μm-0.21 D(v,0.5)μm-2.15 D(v,0.9)μm-4.65			0.74 μm	
Cassava starch	Native	Mean (D)μm-25.2				Cavallini and Franco [42]
	Ball-milled	Mean (D)μm-21.6				
Indica rice starch	Native	Mean (D)μm-4.44				Zhang et al. [24]
	Ball-milled					
	5 h	Mean (D)μm-3.06				
	10 h	Mean (D)μm-2.90				
	50 h	Mean (D)μm-2.14				
	100 h	Mean (D)μm-2.46				
Japonica rice starch	Native	Mean (D)μm-4.16				Zhang et al. [24]
	Ball-milled					
	5 h	Mean (D)μm-2.58				
	10 h	Mean (D)μm-2.19				
	50 h	Mean (D)μm-1.73				
	100 h	Mean (D)μm-1.92				
Glutinous rice starch	Native	Mean (D)μm-5.00				Zhang et al. [24]
	Ball-milled					

(*continued on next page*)

Table 2 (*continued*)

Starch	Ball-milling type	Average granule size (μm)	Span	Average hydrodynamic particle size	Surface area average particle size (μm)/specific area (m^2/g)	References
	5 h	Mean (D)μm-2.71				
	10 h	Mean (D)μm-2.16				
	50 h	Mean (D)μm-1.81				
	100 h	Mean (D)μm-2.18				
Foxtail starch	Native	Mean (D)nm-51,784.89				Jhan et al. [43]
	Ball-mill	Mean (D)nm-467.98				
Sorghum starch	Native	Mean (D)nm-2076.7				Jhan et al. [43]
	Ball-mill	Mean (D)nm-271.12				

D(v, 0.1) and D(v, 0.9) represent the particle diameters with cumulative particle volumes of 10 % and 90 %, respectively; D(v, 0.5), median diameter.
Span: size dispersion index.

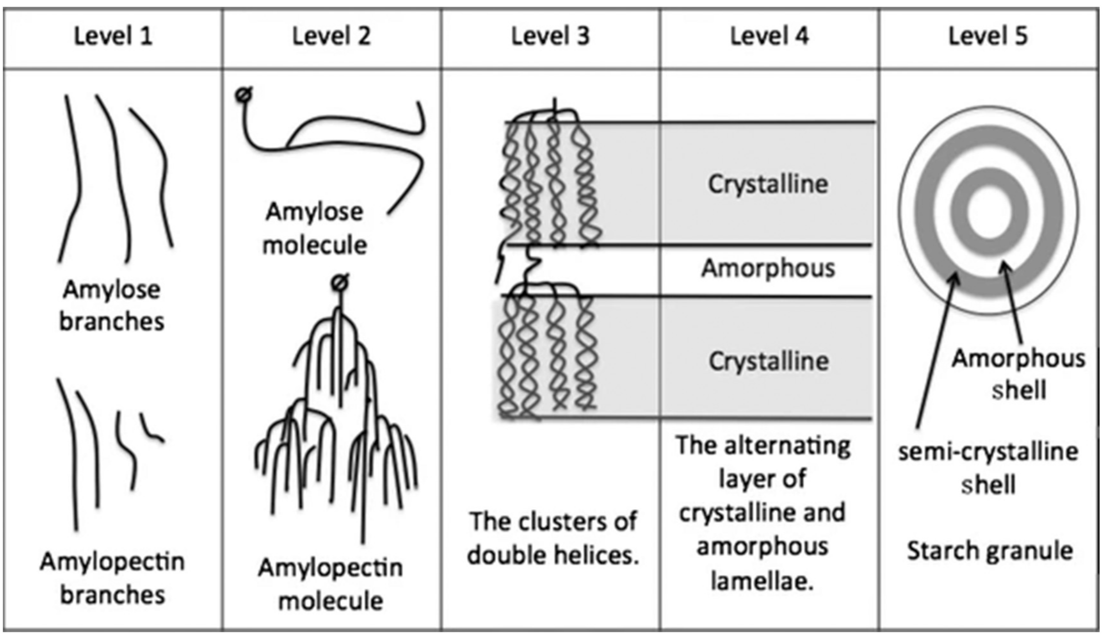


Fig. 2. Schematic diagram of milling damaged starch hierarchical structure.

starches modified with ball-milling at 2.2 J/g and 11 J/g increased to 54 % and 65 %, respectively [5]. This process alters the arrangement of the molecular size of starch and produces smaller weight fractions by amylopectin degradation [24]. These effects may also be responsible for the increased solubility of ball-milled starches due to the physical damage of starch [31].

The ball-milling improves the water solubility index (WSI) and SP of the starch with increased energy supplied in ball-milling. The WSI and SP of rice starch ball-milled by supplying 4.08 kJ/g energy and 85 °C were found between 0.07–29.70 % and 2.12–16.38 g/g [26].

5.3. *Freeze thaw stability*

The freeze-thaw stability is among the most desired properties of modified starches in frozen food items. Syneresis measures the freeze-thaw stability of starch gel after zero to four freeze-thaw cycles [50]. In their studies, He et al. [35] revealed that when corn starch is modified by ball-milling, syneresis is higher than native starch. In addition, ball-milling starch in ceramic pots results in more syneresis than when starch is transformed by ball-milling in stainless steel pots. These findings are most likely the result of severe ball milling altering the structure and characteristics of starch molecules, which led to the loss of crystalline order and double helix content, amylose depolymerization, and amylopectin breakdown in the affected starch granules. The cause of all these events is a drop in the enthalpy and temperature of gelatinized starch, which increases the leaching of free water from corn starch.

5.4. *Water absorption capacity*

Water absorption capacity (WAC) defines the ability of the substance to associate with water under particular conditions. Ball milling of corn starch increased its WAC, which increased as the time for milling increased due to the extremely high surface available and to a loss of highly ordered structures [51]. An increase in the WAC of horse chestnut, water chestnut, and lotus stems is also observed by Ahmad et al. [30]. WAC depends on the molecular structure of the starch, such as the amount of crystalline or amorphous regions and the distribution of granular size, and ball milling disrupts the chains of amylose and amylopectin, exposing the amylose portion of the starch with several binding sites for water absorption. Studies by Moraes et al. [52] also observed an improvement in the WAC of cassava and Peruvian carrot starches after ball milling treatment.

5.5. *Pasting properties*

Pasting involves the swelling of starch granules followed by the secretion of polysaccharides and the final crumbling of starch granules [53–55]. The pasting properties are frequently specified with a rapid visco-analyzer (RVA). The pasting parameters include peak viscosity (PV), trough viscosity (TV), breakdown viscosity (BV), final viscosity (FV), setback viscosity (SV), pasting temperature (PT), and pasting time (Pt).

These variables are influenced by the degree of starch granule damage brought on by the ball-milling processes and the amount of short-chain amylopectin present in the granules. Damaged starch granules hydrate, swell, and leach amylose and amylopectin more readily than undamaged granules, which increases the viscosity of the damaged starch granules [56]. Generally, the short branch-chain starch granules tend to lower PT and PV because of the incapability of the too-short chains to sustain granule rigidity [57].

Among the different methods of starch modification, such as physical, chemical, biological, or combination of methods, physical modification is the most favored because of its simplicity, low cost, and absence of the incidence of chemical or biological means [58]. One of the physical methods, called ball-milling, does not produce co-product and by-products and is known to impact the physicochemical, functional, or especially morphological properties than the other physical modification methods (high-pressure processing, gamma irradiation, microwave, and ultra-sonication). The ball-milling degree of modification depends on the starch type and intensity of the milling. This is connected to structural distortion, morphological flaws, and enhancement in the amorphous phase or subsequent decrease of crystalline domains [10].

Native rice starch (NRS) with moisture, protein, lipid, and ash of 13.7 %, 1.0 %, 0.0 %, and 0.20 % was subjected to the ball-milling process. The pasting parameters of the ball-milled starch were evaluated as depicted in Table 2 [26]. The pasting parameters of PT, PV, BV, TV, SV, and FV decreased as the milling process of mechanical activation increased and continued, like the previous result documented for similar rice starches ([24]). An inverse proportionality relationship was established between ball-milling energy and the following pasting parameters (PV, BV, TV, and FV) [26]. In this work by Gonzalez et al. [26], as the milling energy and time increase, there is a decrease in PV, BV, TV, SV, and FV, but the solubility and SP increase. In the case of PT, the values initially decrease. Still, as the milling energy increases with time, the PT values increase, probably due to agglutination, as the smaller BMS granules clamped or adhered together to form larger particles. These patterns are fairly common in the characteristics of BMSs.

In the study of waxy maize starch (WMS) and waxy rice starch (WRS), it was found that when ball-milled, the PT of the BMSs was lower than native waxy starches. The lower temperatures of the BMSs than the control starches were due to the breakage of the starch granules and the destruction of the crystalline and lamellar structures due to collision, impaction, and impingement action of the milling. Water molecules can easily penetrate the weak and loose structure manifested due to ball-milling. This brief exposition is due to Liu et al. [7]. These disorganized, high entropy, and low enthalpy BMS structures with lower PT are less resistant to the effect of heat, and the granules are easily ruptured when fully swollen with water [10,59,60]. The pasting parameters of BMSs from WMS and WRS decrease as the milling energy intensity increases with time, and various reasons were adduced for this phenomenal decline. A similar process of decline in pasting parameters after ball-milling was reported in corn [25], wheat [61], and rice starches [26].

5.6. Starch retrogradation

Starch retrogradation is a post-gelatinization phenomenon in which starch gel is formed after cooling of heated starch [62]. A favorable condition is provided for retrogradation enhancement by ball-milling. It could be recalled that ball-milling increases the amylose content of ball-milled starches compared to their respective starches. Since the ball-milled starches contain more amylose than native starches, the retrogradation is higher in ball-milled starches (BMS) than in their parent counterparts. Morrison et al. [49] found that amylose was only slightly depolymerized by severe milling (meaning it is resistant to interference).

On the other hand, amylopectin was easily converted at the beginning of milling to low molecular weight fragments (mostly amylose) at all stages of damage, and molecular size was reduced with increased milling time, showing more breakdown of fragments [63]. In their contribution [64], using pea and maize starches by the physical ultracentrifugation method indicated that the attrition process produced granule damage and increased the fragmentation of amylopectin molecules creating amylose-like material and some fragmented AP. Therefore, the amylose seems to resist degradation by the milling process.

Ball-milling of native starches resulted in a decrement of amylopectin due to fragmentation and degradation, with a consequential increment in the amylose content of the BMS. This tends to favor and promote the production of retrograded starches, which are resistant starches with an unquestionable positive health effect. These high-amylose BMS are also good for making noodles and some fermented products. Therefore, there is an increase in retrogradation kinetics due to an increment in damaged starches, which is related to the decrease in the molecular weight of amylopectin [63].

The short-term retrogradation kinetic is controlled by the capability of amylose fractions to align and precipitate. On the other hand, the long-term retrogradation kinetic is influenced by amylopectin. The duration of retrogradation kinetic usually depends on the botanical sources of the starch, the ball-milling time, and the intensity during the production of the starch. The retrogradation kinetics are usually estimated using the Avrami model at various storage times (0, 2, 3, 6, 8, 10, and 15 days) at 4 °C to allow retrogradation to occur [63].

There are mainly two types of retrogradation; short-term amylose retrogradation and long-term amylopectin retrogradation. The preoccupation was previously with the latter. The quantity of water influences the retrogradation in wheat starch gels during aging, but damaged starch also impacts this phenomenon [63]. Further, the increment in damaged starches during milling pivotally increased the degree of amylopectin retrogradation and crystallization rate. It must be noted that documented studies of retrograded ball-milled starches in the literature are rare.

The various starches (low AM starch, high AM starch, and waxy starch) are impacted differently by the grinding process variables and the grinding vessel (stainless steel, ceramic, tungsten, carbide). This is due to the differences in the composition and properties of various starches, further, the grinding vessels generate heat at different rate and intensity. A typical example is a comparative study of the impact of ball-milling of maize starch in ceramic and stainless steel pots [35]. These containers were of the same capacity (500 mL) and filled to 1/3rd of their capacity. The milling conditions were a constant milling speed of 500 rpm for 5 h at a temperature of 5–10 °C to prevent excessive heating of the starch samples. After ball-milling, these authors [35] observed that the cold water solubility (CWS) of maize starch was directly proportional to the milling time of up to 3 h. The real differences between the two containers come into existence following 5 h of ball-milling; CWS increased drastically in the ceramic pot (72.6 %) and the stainless steel pot (70.7 %), as compared to the unmodified maize starches (2.9 %). The implication is that during the ball-milling, the native maize starch losses its semi-crystalline nature and becomes somewhat amorphous with a smaller particle size that enhances CWS. The transparency and freeze-thawed stability of the maize starch improved as CWS increased [35]. It is noted that the container utilized for ball-milling matters as displayed by the ceramic pot and stainless steel pot. The latter is more susceptible to ball-milling conditions than the former.

5.7. Rheological properties

It is important to study the pore sizes, pore volume, and surface area in porous starches created by ball-milling. The different porosities generated due to various milling energy and time during milling have different effects on the granular surface and rheological properties of the BMSs. There are limited studies on the rheology of BMSs. The quantity of energy reserved in a material is called storage modulus (G′), while the amount of energy dissipated is named loss modulus G″ [65]. The G′ and G″ and the loss tangent are associated with the porosity of BMS, and G′ and G″ increase with an increase in temperature.

The rheological parameters of NSs (WCS, LSS, and HCS) and their ball-milled counterparts were studied. All the starch samples displayed high values of G′ and G″ [30]. They observed the viscosities of the BMSs or nanoparticles to be higher than NSs. They stated that the rheological characteristics of starches depend on the shape, size, and dispersion of granules, the amylose content, and granule-granule interaction [66]. The higher viscosity of BMS than NS suspensions has also been reported in corn and cassava after ultra-sonication [67]. During ball-milling, an increase in G' could be due to the expansion of starch granules that increase surface pores and structure; a further increase in temperature depleted the residual crystallites in the BMS with a consequent increase in amorphous region results in decreased G' [68].

Due to its destructive nature on starch granules and the creation of surface pores by mechanical activation, it has been asserted that ball-milling immensely improves the porosity of the granular starch surface and indicates that the milling process could induce the adsorptive potential of starches [36] and mucoadhesive properties [23] in a mucoadhesive polymer.

The studies of the variation in the native and nano-sized millet starch rheological properties were evaluated by G′ and G″. The positive edge of G″ over G′ demonstrated that starch suspension portrays more elastic behavior [38], i.e., they obey Hooke's law; the load is directly proportional to the extension provided the elastic limit is not exceeded. This means the limited cross-linkage in the elastic material prevented permanent flow as long as too strong a force was not applied. The BMSs or the nano-pearl and nano-proso millet starches (PeN and PrN) displayed a higher viscoelastic nature than the control starches, which shows their conventional weak gel performance. These elastic gels can only survive when subjected to small deformation, but the network structures break down when a strong force is applied. This influence of ball-milling on starch materials could be of interest to the polymer industry.

Furthermore, PeN possessed a more enhanced increase nature in viscoelastic than PrN. This behavior was ascribed to the lower hydrodynamic diameter of PeN as particle size straightly influences the rheological behavior of starch. The smaller particle size easily forms particulate associations and displays a more elastic property. The same relationship of the impact of particle size on elasticity was indicated in barley and potato starch nanoparticles [69].

It is pivotal to study further the rheology of BMSs using mechanically activated cassava (MACS) as an example. The effect of the mechanical activation on cassava starch is better comprehended, as depicted in Fig. 5 [41]. According to these authors, the apparent viscosity of the MACS decreases (increase in fluidity) at a constant shear rate as the activation time increases. As shown in Fig. 5, the apparent viscosity decreases drastically at the initial activation period, culminating at zero at 2 h. This decrease in viscosity which amounted to an increase in fluidity, means that the intramolecular and intermolecular bonds holding together the starch chains are weakened, which results in increasing the chain mobility. The decrease in viscosity of the MACS due to mechanical activation means the crystalline domain of the starch granules is further eroded with an increase in amorphism. Certainly, the crystalline region and H-bonding of cassava starch were destroyed during the mechanical activation; its structure became slackened and loose, and rigidity was lost [41].

5.8. Transparency

The study of transparency in ball-milled starches has always been related to its CWS. This is exemplified by maize starch, where there is a direct proportionality relationship between transparency and the CWS of the starch [35]. The latter authors ascribed this co-relationship to the destruction of the crystallinity of the ball-milled maize starch and its conversion to amorphous nature. This means that the symmetry, orderliness, and low entropy of the non-randomly branched amylopectin are further distorted and shattered by the mechanical actions of ball-milling. Furthermore, the increase in amorphousness could be due to an increase in the randomness of the amylose domains and a reduction of associated linearity. The ball-milled maize starch produced could be applied in packaging films due to the transparency and flexibility of its molecular chain due to the generated amorphousness [35]. It must be noted that the attrition, collision, smashing, and shearing actions between the starch granules and the balls of ball-milling equipment bring about the destruction of the crystallinity and its conversion to an amorphous nature.

Investigation into the transparencies of BMCS, BMMS, and their control counterparts were conducted with various milling times at gelatinization temperatures of 30 °C, 70 °C, and 100 °C [44]. Most pivotally, the BMCS and BMMS were more transparent than native starch. This can result from the destruction of the crystalline structure and the conversion of the polycrystalline region to the amorphous region. Additionally, the transparency of the BMCS was higher than that of the BMMS. The reason ascribed to this was the larger size of the starch granules, lower amylose, and its more fragile nature than maize starch granules [44].

6. Characterization of ball-milled starches

6.1. X-ray diffraction analysis (XRD)

The XRD pattern deals with the crystallinity and the amorphism of the native semi-crystalline starch and the consequence of its transformation due to ball-milling. In a study conducted by He et al. [35] to investigate the effect of ball-milling in ceramic and stainless-steel pots using XRD reported that native maize starch (NMS) displayed peaks at 18Ө and 22Ө, purposefully responsible for the semi-crystalline nature of the NMS and its possession of both crystalline and amorphous domains. As the ball-milling time increases, the amorphous regions become larger at the expense of the crystalline region. The cold-water solubility (CWS) increases, causing the diffraction peaks to increase. The development and manifestation of the broad featureless peak of the diffraction spectrum indicate amorphism as the ball-milling time continues and an assertion of the destruction of the crystalline domains. These phenomena favor industrial sectors that prefer fairly amorphous starches rather than extensive crystalline starches. The above expositions reflect the opinions of He et al. [35]. It has been experimentally established that ball-milling has a greater ability to transform semi-crystalline starch to the amorphous state than heat moisture treatment (HMT), ultrasonic deterioration, microwave degradation, and radiation de-polymerization [70].

Pearl millet starch (Pe) and the proso millet starch (Pr) manifested the characteristic A-type polymorph of the cereals (Fig. 3). The ball-milled starches (PeN and PrN) showed no differences in the XRRD pattern but a decreased crystallinity. The factors impacting the crystallinity of various starches are; amylose/amylopectin ratio, the size and shape of the granules, and the exact nature of the complex structure of amylopectin. The reduction in the crystallinity of BMSs was ascribed to the destruction of the amylopectin component and disruption of its branched points with a consequential increase in amorphous domains and amylose content. Certainly, amylopectin is more vulnerable to the milling process than amylose, especially the branch points.

The native potato starch (NPS), the ball-milled potato starch (BMPS), and tea polyphenols (TPs) were studied with XRD. There were manifestations of the B-type XRD pattern and strong peaks at 2θ of 17.1° and a few weak peaks at 5.7°, 15°, 21.8°, and 24° (2θ) for the NPS [71]. In

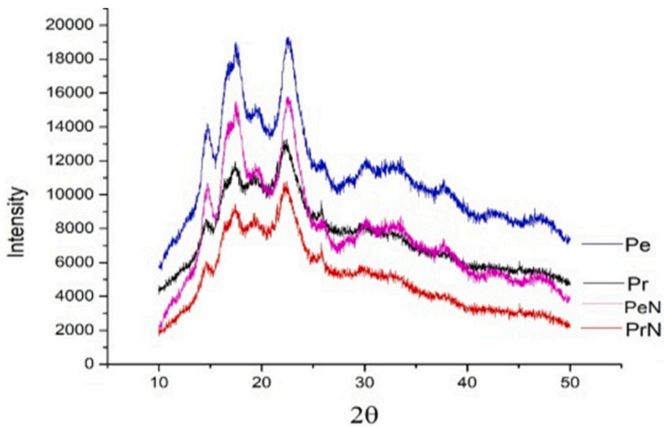


Fig. 3. XRD analysis of native pearl millet starch (Pe), native proso millet starch (Pr), nano pearl millet starch (PeN), and nano proso millet starch (PrN) [38].

contrast, the diffraction pattern of the BMPS differs; it became less acute or partly vanished. This was ascribed to the destruction of the crystal region and the disruption of the starch molecules' intra- and intermolecular hydrogen bonds. The structure of the BMPS becomes weak due to the rupture of the strong intra- and intermolecular hydrogen bonds, and easy water penetration into the starch granules is enhanced. The loose structure is more susceptible to enzymatic hydrolysis, and the reaction with reagents during chemical modification is improved.

6.2. Differential scanning calorimetry

The transformation of native starch from a semi-crystalline state to an amorphous state in excess water, which is an order format to a disorder one, is defined as gelatinization. The gelatinization parameters, onset temperature (To), peak temperature (To), conclusion temperature (Tc), and gelatinization enthalpy (ΔHg) are evaluated by DSC (Table 3).

Ball-milling provides mechanical friction, collision, impingement, and impaction, which alter the functional, physicochemical, structural, and morphological properties of ball-milled starches. This process alters the large semi-crystalline domains into disordered amorphous domains [74]. Hence, the damaged starch granules have a lower gelatinization temperature and enthalpy than the intact granules [75]. Also, small-sized starch granules have higher gelatinization transition temperatures than large-sized ones [61].

In an experiment recently carried out on BMPS, the gelatinization transition temperatures (GTTs) and their ΔHg decreased compared to their native starches (Table 1). The GTTs of the NPS were 49.8, 84.5, and 99.6 °C, and that of ΔHg was 99.4Jg^{-1} [71]. This decrease in the GTTs of the BMS revealed a decrease in crystallinity and increased amorphism. The lower GTTs of BMPS compared to the NPS potato starch is indicative that less energy is required for the initiation of gelatinization of the BMPS. It also suggests that the residual crystallites of the BMPS possessed a lower degree of stability, a consequence of poor packing of residual AP crystallites, and a higher number of morphological flaws and structural defects of the BMPS than the NPS. The lower GTTs of the BMPS also portray the loose nature of its starch and the weaker attractive forces between its starch chains than the unmodified starch. The gelatinization temperature range (R) was calculated for BMPS (Table 3) (95.1–48.9 = 46.2 °C) and for NPS (99.6–49.8 = 49.8 °C) [71]. R-value for NPS is more than that of BMPS which indicates that crystallites of the BMPS have higher crystalline perfection than NPS, which contradicts experimental results. This must be noted, accepted, and ignored because other results support the experimental results (except this latter one); lower GTTs and ΔHg. Three experimental results supported low crystallinity (lower GTTs, ΔHg, and higher R) for ball-milled starch (BMS). Only one result contradicts (low R); the other two parameters (GTTs and ΔHg) still supports the experimental results. Therefore, the BMS is less crystalline when compared to its native starch (unmodified starch).

Just like BMPS, the other ball-milled starches such as mung bean starch [15]; maize starch [40]; buckwheat starch [47] and colored rice starch [37] showed the same To, Tp, Tc, and ΔHg patterns as the BMPS. The differences in these values for the various starches could be due to the peculiar individuality of the different starches, the quantity of water utilized, the ball-milling time, the quantity of amylose and amylopectin in the granules, and the contributory effects of infinitesimal proteins and lipids. For all the starches above, the GTTs and ΔHg decrease as the milling time and intensity increase compared to their native counterparts. The exceptionally high value of ΔHg (131 J/g) for maize starch could be ascribed to the limited water utilized during the gelatinization process (Table 3). The consequence was that the conversion of the semi-crystalline native maize starch to amorphousness was incomplete and some stable starch granules were retained in the ball-milled maize starch, thereby justifying the high enthalpy of gelatinization value.

For example, some values for gelatinization parameters of To, Tp, Tc, and ΔHg for NSs are 40.5 °C, 83.2 °C, 134.5 °C, and 186.7 °C; 58.3 °C, 65.4 °C, 77.9 °C, and 9.4 °C; and 57.9 °C, 66.5 °C, 69.9 °C, and 11.5 °C for maize starch, colored rice starch, and cassava starch, respectively compared to its ball-milled counterparts in Table 3. It is clearly visible that the GTTs and ΔHg of the BMSs were lesser than that of their parent counterparts. This is an indication that ball-milling degraded the structural integrity of the starch granules with a consequential increment of amorphousness and obvious depletion of the crystalline domains.

In a nutshell, some facts about gelatinization in relation to ball-milling are as follows: (i) In the majority of cases, the GTTs and ΔHg decrease as the degree of damaged starches increases, as exemplified by cassava starch [59,60], wheat starch [76] and maize starch [77]; (ii) The energy needed for initiation of gelatinization in BMS is smaller than that for NS, i.e., the amorphous and loose structure of BMS is more heat sensitive than the rather rigid semi-crystalline nature of the NS; (iii) (R) (Tc-To) after ball-milling denotes that every starch granules has been subjected to similar mechanical action.

Table 3
Gelatinization parameters of ball-milled starches.

Starch type	Ball-milling type	Instrument used	Scanning rate (°C/min)	To (°C)	Tp (°C)	Tc (°C)	ΔHg (J/g)	References
Mung bean	–	DSC	10	58.6	66.2	73.9	9.6	Zhang et al. [15]
Potato	Planetary BM	DSC	5	48.9	77.2	95.1	–	Lv et al. [71]
Wheat	–	–	–	56.2	61.2	66.3	11.5	Wu et al. (2017)
Maize	–	–	13	42.9	77	132.7	131	Shi et al. [40]
Wheat	Buhler Lab. mill	DSC	–	57	61.7	66.1	8.9	Yu et al. [47]
Buckwheat	–	DSC	10	67.9	74.2	80.7	12.6	Wronkowska and Haros [72]
Colored rice	–	DSC	10	57.4	64.2	76.5	7.8	Kim and Kim [37]
Cassava	Stirring BM	DSC	10	55.1	64.1	66	5.8	Huang et al. [44]
Rice	–	–	10	64.04	71.60	80.24	8.1	Suksomboon and Naivikul [73]

To, initial temperature; Tp, peak temperature; Tc, conclusion temperature; ΔHg, enthalpy of gelatinization.

6.3. Morphological analysis

The scanning electron microscope (SEM) analysis was conducted for the morphological study of water chestnut starch (WCS), lotus stem starch (LSS), and horse chestnut starch (HCS). The native starch granules were oval or round with smooth or porous surfaces. Morphological flaws developed after ball-milling, and the starch granules were smaller with cracked surfaces [30]. These authors also observed a few large particles, especially the LSS nanoparticles. Furthermore, some granules agglutinate together. This type of structural alteration due to ball-milling has been previously documented for other ball-milled starch granules [35,36]. The formation of the nanoparticles is certainly due to the collision and attrition of the granules with the balls and the mechanical actions involved in the ball-milling process. The frictional force and energy generated during the milling could have been responsible for the agglutination of the powdery starch particles.

The study of native maize starch (NMS) and ball-milled maize starch (BMMS) indicated drastic morphological flaws on the part of the latter. The granular shapes of the NMSs were observed to be polyhedral and uniform surfaces that were a little porous [92]. After ball-milling for 5 h, the NMS granules were physically broken down, and surface smoothness was lost; it became rough, and smaller peeled-off fractions were generated. The different mechanical actions of friction, impingement, compression, shear, attrition, and impaction created coarse granular surfaces with some debris. After ball-milling, the differences between NMS and BMS granules become obvious, as depicted in Fig. 4. There are also discrepancies between the NMS and BMS granules when milling in ceramic and stainless-steel pots. The effect of the milling on starch granules is more drastic in ceramic pots than in stainless steel pots. The NMS was insoluble in cold water, and the granular surface was rigid and not easily penetrated during enzymolysis.

In contrast, the BMS granules were soluble in cold water, and porous surfaces were susceptible to enzyme passage. The destruction caused by ball-milling on maize starch granules was immense; grooves and fissures that had passage to the interior of the granules were displayed on the granular surfaces, and fractures peeled off the main granules creating surface roughness. The above expositions on the impact of ball-milling on maize starch granules are due to He et al. [35].

These processes are similar to those documented by Dhital et al. [78]. These authors hypothesized that; starch granular surface fissures and grooves enhanced enzymatic hydrolysis and improved enzyme diffusion into the interior of the granules; fragments possession of more surface area per unit mass and therefore increased the rate of reaction in relation to enzymatic hydrolysis; ball-milling is good pretreatment before enzymolysis.

A morphological study of the effect of ball-milling on native proso and pearl millet starch granules shows that the large, oval, and polyhedral granules with smooth surfaces after ball-milling were converted to elliptical, irregular shape granules with rough surfaces [38]. These authors asserted that ball-milled starch granules were partially impaired, though some large granules persist after the milling. Similar phenomena were documented for horse chestnut starch, lotus stem starch, water chestnut starch granules [30], and maize starch granules [35] after ball-milling for size reduction. The morphological alterations of the starch granules resulting from ball-milling will change all properties, including physicochemical, functional, pasting, rheological, and thermal. Furthermore, there are many advantages associated with these starch nanoparticles for food and non-food applications. These nanoparticles possess a high surface-to-area ratio, improved surface reactivity of hydroxyl groups, enhanced long storage stability, and altered thermal and rheological attributes [79].

Similar results were obtained when NPS was subjected to 1 h of ball-

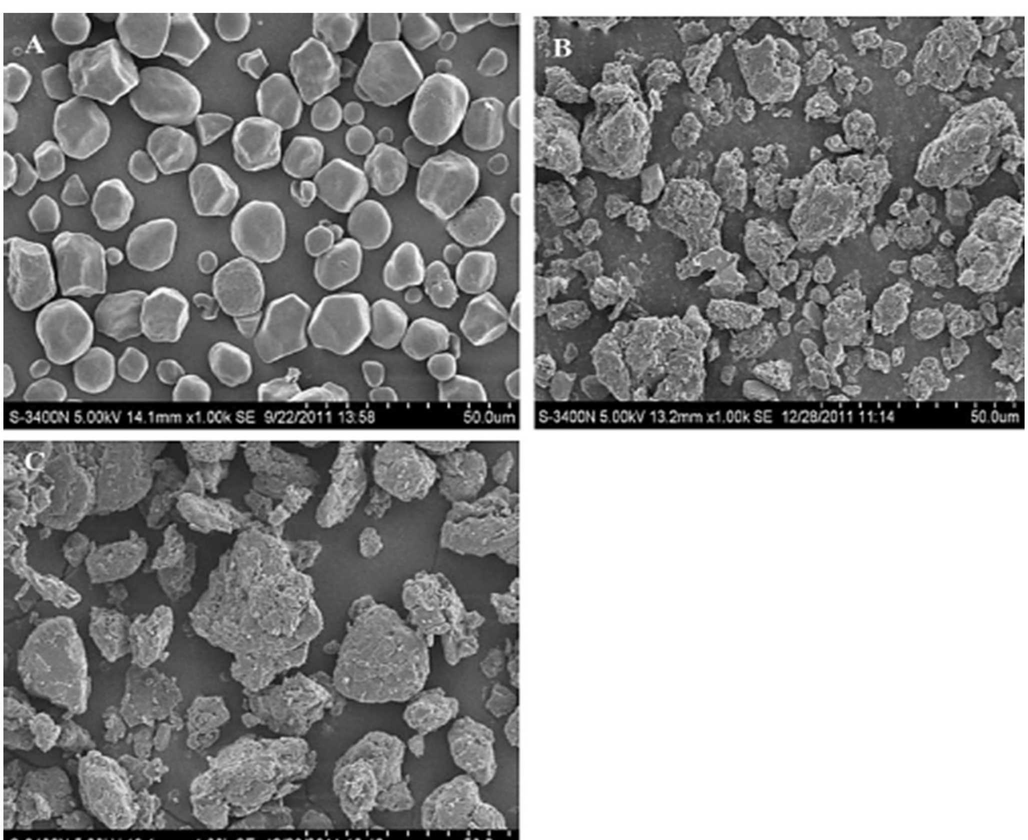


Fig. 4. Scanning electron micrography (SEM) of (A) Native maize starch, (B) ball-milled maize starch (in ceramic pots), and (C) ball-milled maize starch (in stainless steel pots) [35].

milling. The previous regular oval shapes and size (20-100 μm) of the NPS granules were altered to irregular shaped granules with rough surfaces [71]. An increase in the ball-milling time to 3 and 9 h, and the starch granules were finally damaged, and this was ascribed to the frictional and impaction forces of the balls in rice starch granules [24].

6.4. FTIR analysis

To study the functional groups and other associated groups, NPS, BMPS, and the effect of tea polyphenols on BMPS (BMPST) were evaluated using FTIR. The FTIR spectrum of the NPS displayed the 3452 cm^{-1} band for the OH stretching and was connected to the intra- and intermolecular H bonding (Fig. 6). The knife-like edge band at the 2939 cm^{-1} region is attributed to methylene ($-CH_2$) bonds and peaks at 1665 cm^{-1} in NPS allotted to scissoring vibration of two OH bonds of mopped water molecules [80]. Furthermore, bands at 1167 and 1080 cm^{-1} were solely ascribed to anhydroglucose rings stretching of C-O-H in starch [81]. A good corroboration with the X-ray diffraction stated that the steeply ordered crystalline region of starch was smashed by the milling is the fact that the peak intensity between 3600 and 3000 cm^{-1} in BMPS was diminished after 7 h of milling (Fig. 6) [71]. As depicted in the spectrum of BMPS (Fig. 5), 2939, 1665, and 1167 cm^{-1} bands of the NPS switched to 2926, 1646, and 1163 cm^{-1}, respectively. In contrast, in BMPST, the bands at 2939 cm^{-1} and 1167 cm^{-1} of the NPS were switched to 2928 cm^{-1} and 1156 cm^{-1}, respectively. This treatment could damage the crystal structure of the starch granules, thereby exposing more hydroxyl groups in the starch chains [82] for more reactions. Ball-milling is a good pre-treatment before chemical or enzymatic modification. It is also presumably possible for the TPs to be in between starch chains via H-bonds because of the abundantly exposed OH groups, resulting in a new low-order crystalline structure [83]. It is to be noted that ball-milling is a good pre-treatment for dual heterogeneous modification and dual homogeneous modification (Table 4).

7. Applications of ball-milled modified starches and nano starches in the food

The ball-milled starches find widespread applicability in various food systems due to their enhanced functional properties. The ball-milled starches could be used as emulsifying agents, fat replacers, and wall materials to encapsulate desired compounds, among other applications. The important applications of ball-milled starches are summarized in Table 5.

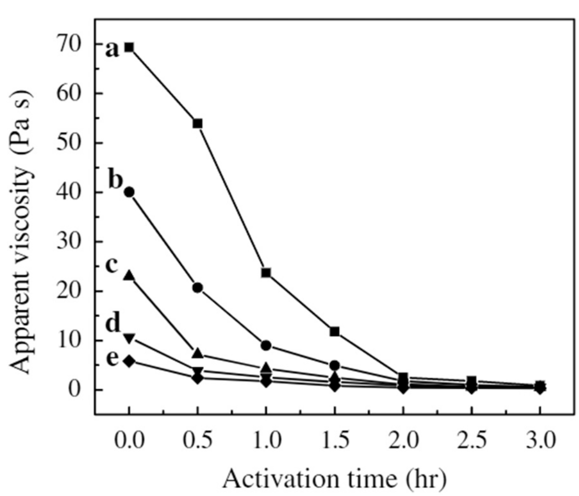


Fig. 5. Aparent viscosity of mechanically activated cassava starch at different shear rates: (a) 0.05 s^{-1}, (b) 0.25 s^{-1}, (c) 1.00 s^{-1}, (d) 2.50 s^{-1}, and (e) 5.00 s^{-1} [41].

7.1. Emulsification

The ball-milled starches possess great emulsification capacity and give increased stability to the emulsions. Liu et al. [88] used the taro ball-milled starch separately and in combination with octenyl succinic anhydride esterification for its suitability in forming and stabilizing oil in water emulsion. The use of ball-milled and ball-milled esterified starch resulted in decreased surface tension and increased emulsion viscosity. The reduction in surface tension is due to interface coverage by the extremely increased surface area of small particles with irregular shapes and fragments produced from the damage of starch molecules from ball-milling. The increased viscosity of the emulsion is desirable as it slows down the movement of particles and reduces the collision between emulsion droplets to maintain emulsion stability.

The applicability of ball-milled maize starches in emulsion formation and their stability was explored by Lu et al. [89]. The stabilizing potential of milled maize starch particles steadily improved with the prolonged treatment duration. The improved stability of emulsions due to milled starches could be related to the availability of more starch particles in interfacial areas because of mechanical damage triggered by the milling process.

7.2. Encapsulation

Many materials, including starches, maltodextrins, and hydrocolloids, have encapsulated and protected the compounds from degradation during processing and storage [85]. The ball-milled starches have high encapsulation efficiency, evidenced by the positive impact of treatment starch on the retention of beta-carotene. The ball-milled rice starch and gelatin also protected the beta-carotene structure. This produced a maximum encapsulated beta-carotene amount (0.154 mg/g), about 4 times more than encapsulation with native rice starch [13]. Roa et al. [85] employed the amaranth starch enriched fraction to encapsulate beta-carotene after dry and wet ball-milling. The ball-milled starch-enriched amaranth fractions displayed higher beta-carotene encapsulation efficiency and stability. The encapsulated beta-carotene content increased to 2.46 mg/g starch using ball-milled starch-enriched fractions over 0.33 mg/g beta-carotene encapsulated by native starch. The higher encapsulation efficiency of ball-milled materials could be attributed to milling induced degradation of amylopectin in small-size molecules [90], which hastened the development of inclusion complexes of starch and beta-carotene. However, Ahamd et al. [84] found that the ball-milled starch particles used to encapsulate probiotics derived from camel milk are ineffective for encapsulation. They result in decreased viability of cells.

7.3. Fat replacer

The ball-milled starches could be used as fat replacers in various foods, including ball-milled corn starch in cream. The results indicated that the ball-milled starch increases the cream viscosity and reduces water mobility. The ball-milled starch at a low-fat replacement level (up to 20 %) displayed a positive impact on the quality of the cream. It was observed that the different proportions of micronized starch addition had no significant impact on the cream overrun in the 1st stage of whipping (1 min); however, the overrun increased significantly in the 2nd stage (2–4 min). Cream overrun decreased with whipping beyond 5 min, possibly due to the coalescence of small particles and the formation of larger aggregates. This study, therefore, outlined that the micronized corn starch prepared by acidification and ball-milling could be effectively used as a fat replacer. The cream with better foaming and storage stability can be obtained by replacing 15 % of its fat with micronized starch [87].

Table 4
Pasting characteristics of various ball-milled starches.

Starch type	PV (cP)	TV (cP)	BV (cP)	SV (cP)	FV (cP)	PT (°C)	References
Waxy maize	1351	55.87	791.5	272.4	832.26	68.72	Liu et al. [7]
Waxy rice	664.53	511.11	153.42	455.65	967.51	63.63	Liu et al. [7]
Rice	4384	3384	1006	2386	5764	79.1	Gonzalez et al. [26]
Wheat	2260	1780	2627	830	480	92.8	Wu et al. (2017)
Maize	1398	1229	167	310	1539	84.4	Shi et al. [40]
Wheat	1635	1310	325	526	1836	90.9	Yu et al. [47]
Buckwheat	1531	1431	100	1489	2919	61.9	Wronkowska and Haros [72]
Wheat	380.3	321.6	58.7	15.9	476.5	77.6	Barrera et al. [56]

PV-peak viscosity; TV-trough viscosity; BV-breakdown viscosity; SV-setback viscosity; FV-final viscosity; PT-pasting temperature; 1 cP = 1 mPa·s = 0.4762 Bu (Conversion factor).

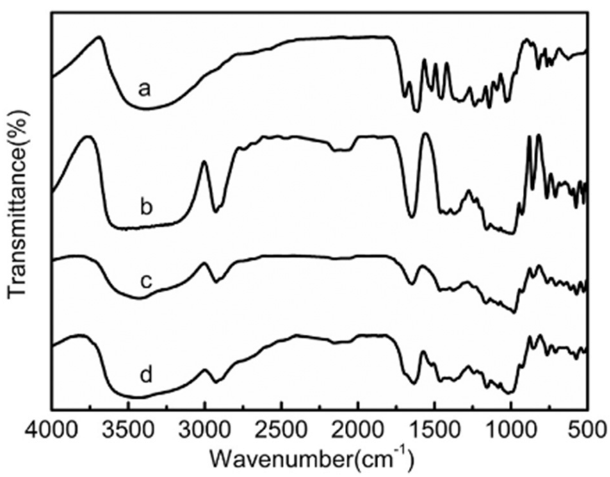


Fig. 6. FTIR spectrum of (a) tea polyphenolic content, (b) potato starch (no treatment) (c) ball-milling of starch (milling time-7 h), and (d) ball-milling of starch with tea polyphenols (tea polyphenols/native potato starch:1/10, *w*/w: milling time-7 h) [71].

7.4. Noodles

Flour containing more damaged starch due to ball-milling had high water absorption, and noodles prepared from such flour had increased breaking stress [86]. The average water absorption increased by about 4.5 %, 10 %, and 15 %, and the breaking stress was increased by about 5 %, 9 %, and 16 % after 8, 16, and 24 h of ball-milling. The high starch damage in ball-milled flours produced noodles with relatively low firmness, as is evidenced by their low cutting stress and surface firmness.

8. Conclusions

Ball-milling reduces the starch to nano-size by its action of mechanical activation, collision, frictional, and impaction forces. Ball-milling action enhances easy water percolation into the starch molecules with rapid swelling. The oxidative effect of ball-milling in the wet medium converts hydroxyl groups (OH) into carbonyl and carboxyl groups is similar to the hypochlorite oxidation products of starch. This chemical reaction of ball-milling is worth noting. Ball-milling could be used to modify starch properties such as gelatinization temperature, viscosity, and retrogradation, to improve the starch functionality in food products, such as texture, stability, and shelf life. Further, milled starch nanoemulsion has the potential to improve the solubility, stability, and bioavailability of vitamins and flavors. Also, generating high amylose starches by ball milling produces resistant starches and as a good starting material in producing edible films and coatings. Literature reported several applications of ball-milled starch, such as coatings, edible films, low-fat products, baked products, nanocarriers, and functional gels.

Table 5
Applications of ball-milled starches in different food systems.

Ball-milling	Starch	Food system	Major findings	References
Planetary	Water chestnut	Camel milk-derived probiotics	• Encapsulation of probiotics with ball-milled starch nano-particles decreased the viable cell count • Increased bioactivity	[84]
planetary	Rice	Beta-carotene	• Four times increase in encapsulated beta-carotene • >86 % encapsulated beta-carotene content • Improved encapsulation performance	[13]
Planetary	Amaranth	Beta-carotene	• Three times more beta-carotene retention than native-starch	[85]
Ceramic cylindrical grinding stone	Wheat	Noodles	• Increased breaking stress of noodles • Low cutting stress and surface firmness • Less firm noodles	[86]
Planetary	Corn	Cream	• Increased cream viscosity and decreased the mobility • Increased overrun in the second stage (2–4 min) of whipping cream	[87]
Planetary	Areca taro	Emulsion	• Increased emulsion stability • High surface activity and emulsion stability • Prevented coalescence of droplets	[88]
Planetary	Maize	Emulsion	• Increased emulsion stability with an increase in time • High amylose milled maize starches are more efficient than milled waxy maize starch for providing emulsion stability	[89]

Presently most of the work done on starch modification via ball-milling technique is through planetary ball-mill; thus, in the future, more research should focus on tumbling, vibratory, and attrition ball-mills so that the variability in the modification of starch properties should be summarized and compared to evaluate the best ball-mill type for efficient starch modification. Also, starches from various botanical sources and origins should be evaluated for suitability in preparing modified starches and starch nanoparticles. Also, more research should focus on the milling time, energy, and starch concentration to obtain their specific applications in liquid or creamy systems of interest to food applications to produce novel food ingredients and improve the functionality of existing ones, and extract bioactive compounds.

Declaration of competing interest

No.

Data availability

The authors do not have permission to share data.

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