

## RESEARCH ARTICLE

# Material properties of partially pregelatinized cassava starch prepared by mechanical activation

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This study has focused on the preparation of partially pregelatinized cassava starch (PPCS) by mechanical activation (MA) using a customized stirring ball mill. The changes in degree of gelatinization, crystal structure, particle size, surface morphology, powder characteristics, and pasting properties of cassava starch mechanically activated for different time were investigated by various characterizations. The results showed that MA could significantly destroy the crystal structure of starch granules, contributing to the increase of cold-water solubility, flowability, and floodability, the variations of particle size and surface morphology, and the decrease in pasting temperature, viscosity of cooked PPCS paste, breakdown, and setback. It was also found that the PPCS with different degree of gelatinization could be prepared by controlling the milling time. With the unique properties induced by MA, the potential use of PPCS as excipient in pharmaceutical formulations is discussed.

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## 1 Introduction

Starch, a primary carbohydrate polymer, plays an important role in the food industry and it is also used as raw material to prepare different products in other industries [1–3]. In pharmaceutical industry, starch and its derivatives are employed as multipurpose excipients in various solid dosage forms, especially as disintegrants, fillers, and lubricants in powder form and as binders in paste form in tablet formulation [4–7]. Starch is mainly produced from grain crops such as corn, wheat, and rice. Due to increasing shortage of foods all over the world, the use of non-staple

food crops for starch production has attracted more and more attention. Cassava, a shrubby tropical plant grown for its large, tuberous, starchy roots, is an important cash crop in tropical countries because it has the remarkable capacity to adapt to various agro-ecological conditions, such as marginal lands where other agricultural crops cannot grow well [8–10]. Cassava starch possesses a variety of interesting properties, like low gelatinization temperature, clarity, and bland taste, which make it desirable for food and nonfood industries applications [11]. However, native cassava starch has some negative characteristics, such as poor flow properties, high cohesiveness, and sensitivity to shear, high temperature, and low pH, which reduce its uses in many fields [12]. These shortcomings can be overcome by starch modification, including chemical, physical, and enzymatic methods [13, 14]. Typical physical modifications are pregelatinization, annealing, and heat-moisture treatment. Among these methods, pregelatinization, which leads to irreversible granule swelling, loss of birefringence and crystallinity, is usually used for the modification of various starches, and the resulting products are called pregelatinized starches (PS). Unlike native starches, PS can swell in cold water

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**Abbreviations:** BU, Brabender unit; FPS, fully pregelatinized starches; MA, mechanical activation; PPCS, partially pregelatinized cassava starch; PPS, partially pregelatinized starches; PS, pregelatinized starches; S<sub>c</sub>, cold-water solubility

and are capable of forming gel barriers, and possess better flow and compaction properties [15, 16].

Functionally, PS are split into two groups, fully pregelatinized and partially pregelatinized. Fully pregelatinized starches (FPS) are being used as binders in pharmaceutical formulations and as major ingredients, bulking agents, or thickening agents for many food products [17]. But due to the gelatinization, much of the disintegration properties are lost. On the other hand, partially pregelatinized starches (PPS) have a mixture of properties of both native and fully gelatinized starches, which makes them useful as both a binder and a disintegrant in tablet formulation. Moreover, starches could possess better flowability and compaction characteristics after modification [5]. Therefore, PPS can be utilized as pharmaceutical excipients in a variety of applications, including direct compaction, wet granulation, fluid bed granulation, and capsule plug formulation.

Excipients may determine the quality of a formulation and in many cases the bioavailability of drug from tablets, and the required degrees of gelatinization of starches are different for different drugs and must be strictly controlled. So, it is important to prepare the PPS with different required degrees of gelatinization. Traditionally, PS are mainly produced by thermal modification, such as extrusion, drum drying, spray drying, and other relatively complex techniques [16, 18, 19]. In these cases, starch gelatinization is carried out in watery suspension. In addition, it is difficult to control the required degrees of gelatinization of PPS by these methods.

Mechanical activation (MA), usually carried out by high-energy milling, refers to the use of friction, collision, impingement, shear, and other mechanical actions to change the physicochemical properties of the solids [20, 21]. When subjected to enough mechanical energy, the chemical bonds in solids can be effectively broken up, along with the collapse of their crystal structure, phase transformation, and the changes in surface characteristics [1, 22]. In addition, a part of mechanical energy is converted into thermal energy which can also affect the physicochemical properties of the solids, especially the polymers. Currently, MA has been widely used in various fields, such as extractive metallurgy, crystal engineering, nanomatrix composites, agriculture, pharmacy, waste disposal, organic material synthesis, and so on [23–26]. In our previous studies, MA has been successfully used for the pretreatment of starches, sugarcane bagasse and cassava stillage residue, and the results showed that MA could significantly change the crystalline structures and physicochemical properties of these solid materials and thus enhance their chemical reactivity [27–30]. Compared to other pretreatment methods, MA is a simple and environmentally friendly procedure relying on simple and cheap equipment and can be operated

without the use of solvents, intermediate fusion, etc. [31]. Hopefully, MA can be used to produce PPS with required degrees of gelatinization by controlling the milling time. For the potential applications of PPS in pharmaceutical formulations, it is important to know their material properties, which has significant impact on the production efficiency and quality of pharmaceutical products.

In this work, MA was applied to prepare partially pregelatinized cassava starch (PPCS) with different degree of gelatinization, and the particle size, crystal structure, morphology, powder integrative characteristic, and pasting properties of PPCS were determined using particle size analyzer, XRD, SEM, powder comprehensive characteristics tester, and Brabender viscoamylograph, respectively. Furthermore, the potential use of PPCS as excipient in pharmaceutical formulations is also discussed.

## 2 Materials and methods

### 2.1 Materials

Cassava starch (moisture content = 12–14%), food grade, was obtained from Minyang Biological Inc., Ltd. (Guangxi, P. R. China). All other chemical reagents were of analytical grade without further purification and were obtained commercially, and deionized water was used throughout the work.

### 2.2 Mechanical activation of cassava starch

PPCS was prepared by MA, which was performed in a customized stirring ball mill driven by a commercial available drill press (maximum drilling diameter = 16 mm) equipped with a speed-tuned motor [28]. For each milling experiment, native cassava starch sample (80 g in each batch) was added into a stainless steel chamber (1200 mL) with 300 mL zirconia milling balls (6 mm-diameter), then the sample was subjected to dry milling at a fixed temperature of 50°C and no other additives were used during milling. The balls were removed after the sample was milled for different designated time (10, 20, 30, 60, 90, 120, 150, and 180 min), then the chamber and milling balls were thoroughly cleaned and dried before the next milling experiment. The resulting samples were sealed in plastic bags and stored in a silica-gel desiccator.

### 2.3 Cold-water solubility

The cold-water solubility ( $S_c$ ) of starch samples was measured as follows: about 2.0 g of sample was dissolved in 100 mL water at a constant temperature (30°C) for 20 min in a DF2101B thermostatic magnetic stirrer (Gongyi Yuhua Instrument Co., Ltd., P. R. China), with

continuous magnetic stirring in order to avoid agglomeration. Then the solution was centrifuged at 1309g for 20 min by an 802B table-top centrifuge (Shanghai Anting Scientific Instrument Co., Ltd., P. R. China). Twenty-five milliliters of supernatant was removed and placed in a drying oven at 110°C to a constant weight. The  $S_c$  of starch samples was calculated using the following equation:

$$S_c = \frac{m_2 \times 4}{m_1} \times 100\% \quad (1)$$

where  $m_1$  is the total dry weight of starch sample,  $m_2$  is the dry weight of 25 mL of starch supernatant.

## 2.4 XRD analysis

XRD analysis of the starch samples was performed on a Rigaku D/MAX 2500 V diffractometer (Japan) using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 30 mA, with a step size of 0.02° and a recorded range from 10° to 40°.

## 2.5 Particle size analysis

The particle size distributions of starch samples were determined by using an SA-CP3 particle size analyzer (Shimadzu, Japan). Ethanol, used as dispersing agent, was added to the sample which was then ultrasonically dispersed for 2 min, and then the suspension was immediately subjected to particle size analysis.

## 2.6 Morphology observation

Morphologies of different starch samples were performed using an S-570 SEM (Hitachi, Japan). The sample was fixed on a sample bench using a double glue tape, and then a thin layer of gold was coated on the sample prior to measurement to improve the conductivity. SEM micrographs with different magnifications were obtained to observe the surface morphologies of different samples.

## 2.7 Powder characteristics testing

The powder characteristics indices of the starch samples, such as angle of repose ( $\theta_r$ ), angle of fall ( $\theta_f$ ), bulk density ( $D_b$ ), tapped density ( $D_t$ ), voidage ( $\epsilon$ ), and dispersibility, were measured by a BT-1000 powder comprehensive characteristics tester (Dandong, P. R. China) according to the operating instruction. In addition, angle of difference ( $\theta_d$ ), compressibility ( $C_p$ ) could be calculated according to the obtained characteristics indices [32]. The angle of difference is the difference between the angle of repose and angle of fall ( $\theta_d = \theta_r - \theta_f$ ). The compressibility was

obtained by following calculation:

$$C_p = \frac{D_t - D_b}{D_t} \times 100\% \quad (2)$$

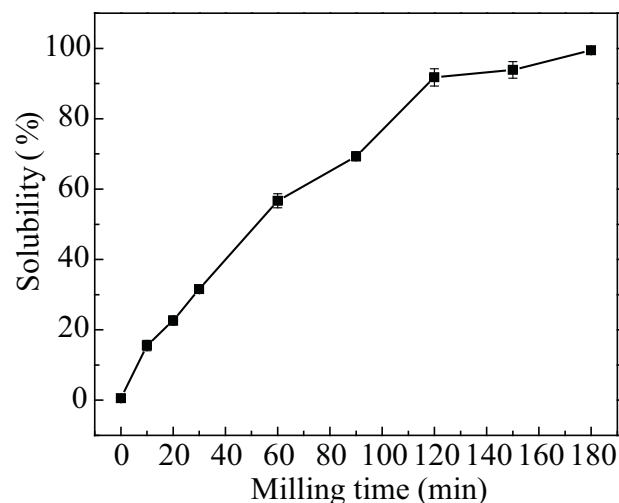
## 2.8 Pasting properties

Pasting characteristics of 6% starch slurries (dry matter basis) were measured using a Brabender Viscoamylograph (Brabender Viscograph-E, Germany) equipped with a 700 cmg sensitivity cartridge operated at a speed of 75 rpm [33]. The slurry samples were heated from 45 to 95°C at a rate of 2°C/min, held at 95°C for 30 min, cooled down to 50°C at a rate of 2°C/min, and held for 30 min at 50°C. The viscosity profile indices recorded included the following: pasting temperature, peak viscosity, viscosity at 95°C, viscosity after 30 min hold at 95°C (95°C-hold), viscosity at 50°C and viscosity after 30 min hold at 50°C (50°C-hold). In addition, the breakdown (=peak viscosity – viscosity at 95°C-hold) and setback (=viscosity at 50°C – viscosity at 95°C-hold) were also calculated.

## 3 Results and discussion

### 3.1 Effect of milling time on the degree of gelatinization of cassava starch

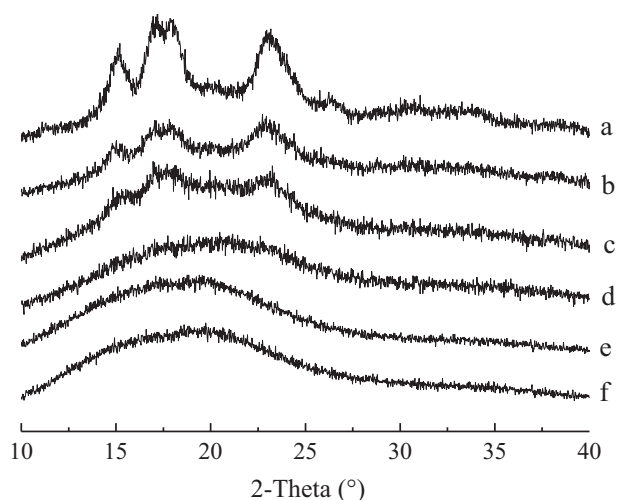
The solubility of starch in cold water is an evaluation criterion for the degree of gelatinization of starch, and the greater  $S_c$  indicates the higher degree of gelatinization. The effect of milling time on  $S_c$  of cassava starch is presented in Fig. 1, which shows that the degree of



**Figure 1.** Effect of milling time on the cold-water solubility of cassava starch.

gelatinization of PPCS increased with the increase of milling time. The  $S_c$  of native cassava starch was only 0.6%, but reached to 31.6, 56.7, and 91.8% after mechanically activated for 30, 60, and 120 min, respectively. It also can be observed that  $S_c$  of PPCS approximately increased linearly as increasing the milling time from 0 to 120 min, indicating that the degree of gelatinization of PPCS could be controlled by milling time. XRD spectra of cassava starch with different milling time are presented in Fig. 2. The spectrum of the native cassava starch shows definite diffraction peaks, which reflect crystalline regions in the starch. As the increase of milling time, the decrease in diffraction pattern and the broadening of diffraction peaks can be clearly observed. After activated for 120 min, the peak diffraction disappears completely, implying that cassava starch has been converted largely into non-crystalline states. During the processing of MA, strong mechanical actions between milling balls destroyed the starch granules repeatedly, resulting in the destruction of stable starch structure and the degrading of crystalline regions [34]. The damage of starch granules and the increase of amorphization allowed greater entry of water into the interior of the granules, which could improve the solubility of starch. The longer milling time contributed to greater disruption of crystal structure of starch granules, which is responsible for the gelatinization of starch [35]. So, MA is an effective and simple method for the preparation of PPCS with different degree of gelatinization by controlling the milling time.

Cassava starch is composed of two polymers, amylose and amylopectin which are tightly bound in crystal structure. Through the process of MA with controlled milling time, the stable structure of starch granules could be



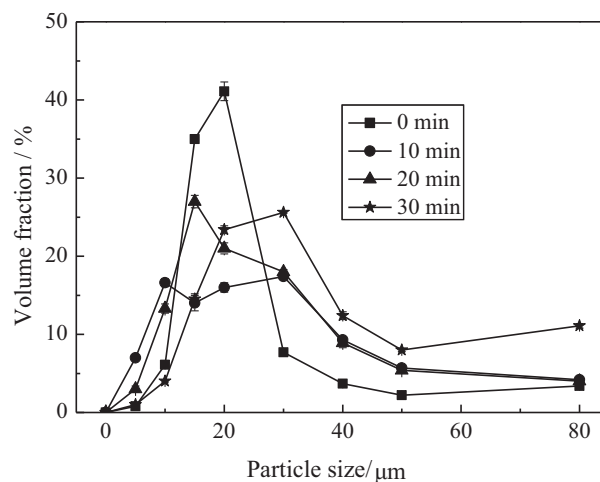
**Figure 2.** XRD patterns of native cassava starch and PPCS with different milling time. (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 60 min; (f) 120 min.

damaged partially, resulting in partial cold-water solubility. In granulation applications, PPCS exhibits dual functionality as both binder and disintegrant as a result of partial cold-water solubility. With the property of partial solubility in cold water, PPCS can reduce the processing cost by eliminating the time and expense of preparing traditional binder solutions. It was found that the PPCS with greater degree of gelatinization (milling time >30 min) was difficult to be granulated. In addition, the suitable  $S_c$  of PPS used for excipient is about 20%. So, the material properties of PPCS with milling time no more than 30 min are mainly investigated and discussed in the following.

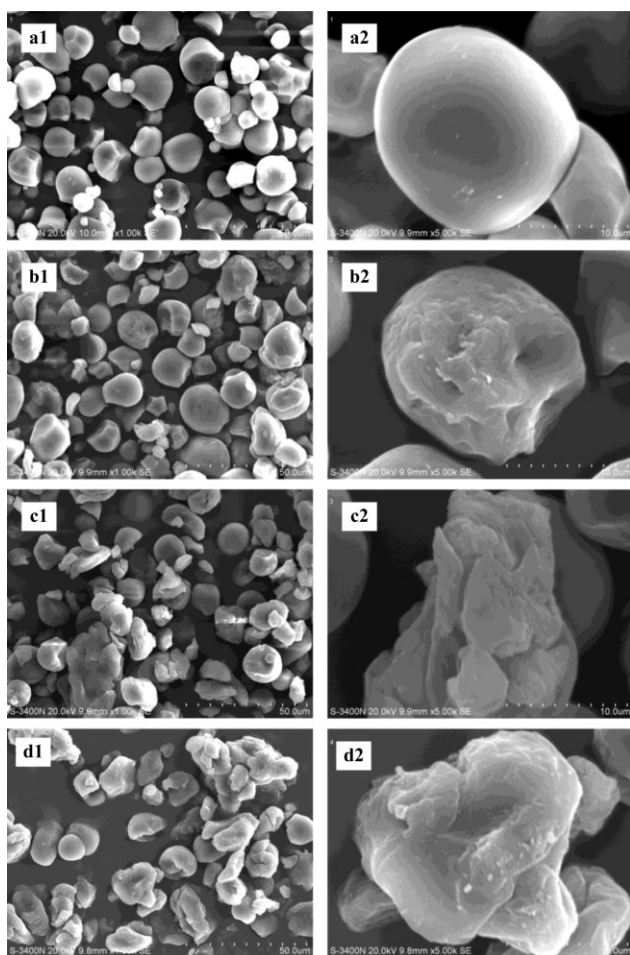
### 3.2 Particle size and morphology

The size distribution data and SEM micrographs of native cassava starch and PPCS samples with different milling time are shown in Figs. 3 and 4, respectively, from which it can be seen that MA has great effect on the particle size and morphology of cassava starch. It indicates that the particle size of cassava starch decreased when subjected to MA, and then it set back to larger with the increase of milling time. In the early stage of MA, the size reduction of starch granules was mainly occurred by intensive mechanical milling. However, as the milling time increased, starch granules were continuously damaged, leading to the increase of amorphous phase and greater water penetration and agglomeration via the interaction between the greater amorphous regions, which thus increase the particle size of starch granules [27]. After milled for 30 min, the destruction and agglomeration of starch granules became significant, resulting to the obvious increase of particle size.

The changes of starch granules before and after MA can be observed clearly from the SEM images (Fig. 4).



**Figure 3.** Particle size distribution of native cassava starch and PPCS with different milling time.



**Figure 4.** SEM micrographs of native cassava starch and PPCS with different milling time at different magnifications. (a1 and a2) 0 min; (b1 and b2) 10 min; (c1 and c2) 20 min; (d1 and d2) 30 min.

Native cassava starch granules are essentially spherical with smooth surfaces, which can be seen in Fig. 4a1 and a2. When subjected to MA for 10 min (Fig. 4b1 and b2), the starch granules appear to be damaged and fractured,

contributing to the generation of rough surfaces and small irregular particles. As the milling time increased, the structure of starch granules continued to be destroyed, losing their initial shapes gradually. After milled for 30 min (Fig. 4d1 and d2), the starch granules become prolate and irregular, with quite rough surfaces, and the irregular congregates consisting of damaged starch granules are easily formed during intensive milling. The damage of starch granules and increase of amorphization can improve the rate of moisture entry, which is widely recognized as the primary step in the disintegration and deaggregation processes of tablet and granules, respectively [4]. As a result, the destruction of starch granules has an indirect effect on drug dissolution from solid dosage forms.

### 3.3 Powder characteristics

In order to investigate the powder characteristics of native cassava starch and PPCS samples with different milling time, the powder comprehensive characteristics tester was applied to measure different powder characteristics indices, and then the flowability and floodability of PPCS could be determined and discussed. Angle of repose and angle of fall can directly reflect the flowability of powder, and the lower values of angle of repose and angle of fall mean better flowability. Compressibility is also related to the flowability of powder. The greater the compressibility of powder, the less flowable it is [36]. The floodability shows stability or instability of a powder and so the ease with which it flows under strain. The floodability of powder is obtained from angle of difference and dispersibility, and the higher values of angle of difference and dispersibility, the greater flushing tendency in the behavior of the powder [32, 37]. Particles with sufficiently high flowability and floodability would be easy to handle, resulting in uniform bulk properties.

Based on the experimental results, the flow characteristics of native cassava starch and PPCS powder with different milling time are presented in Table 1. It shows that the increasing MA time led to a decrease in angle of

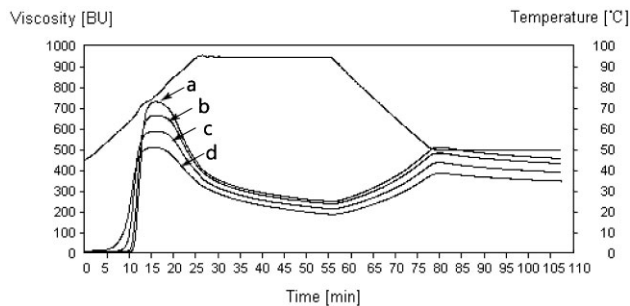
**Table 1.** Powder characteristics of native cassava starch and PPCS with different milling time<sup>a)</sup>

Milling time (min)	Angle of repose (°)	Angle of fall (°)	Angle of difference <sup>b)</sup> (°)	Dispersibility (%)	Voidage (%)	Bulk density (g/mL)	Tapped density (g/mL)	Compressibility <sup>c)</sup> (%)
0	48.3 ± 0.6	21.7 ± 1.1	26.6	43.6 ± 0.3	46.0 ± 0.8	0.56 ± 0.02	0.82 ± 0.03	31.7
10	46.8 ± 0.9	19.2 ± 0.7	27.6	44.3 ± 0.3	48.0 ± 1.1	0.55 ± 0.00	0.81 ± 0.03	32.1
20	43.5 ± 0.8	14.8 ± 0.9	28.7	45.9 ± 0.5	52.0 ± 0.5	0.53 ± 0.01	0.70 ± 0.04	24.3
30	41.2 ± 0.6	11.2 ± 1.0	30.0	46.0 ± 0.4	54.0 ± 0.6	0.54 ± 0.03	0.68 ± 0.01	20.6

a) Means of three replicates ± SD.

b) Angle of difference = angle of repose – angle of fall.

c) Compressibility (%) = (tapped density – bulk density)/tapped density.



**Figure 5.** Viscosity and temperature profiles of native cassava starch and PPCS with different milling time. (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min.

repose, angle of fall and compressibility, and an increase in angle of difference, voidage, and dispersibility, resulting in the increase of flowability and floodability of the starch granules. It should be noted that the flowability depends on the particle size, its morphology and distribution. As shown in Fig. 4, the starch granules were destroyed and agglomerated to larger irregular particles after MA, leaving more voids between the particles and thus decreasing the friction, which are mainly accounted for the increased flowability of milled cassava starch. Furthermore, during the processing of MA, a part of electrostatic force among these granules could be eliminated under the strong milling, which also resulted in better flowability of starch granules. The powder that gives rise to floodability is usually fine and has large voidage, because the particles can build a weak structure of relatively large voidage by the cohesive force between particles [38]. MA destroyed the starch granules, causing the agglomeration of damaged starch particles, which leads to the increase of voidage. Therefore, the milled cassava starch exhibited better floodability. Undoubtedly, PPCS provides better flow properties, demanded by today's high-speed tableting and capsule filling equipment, ensuring that manufacturers can produce tablets and capsules with consistent uniform weight and drug content.

### 3.4 Pasting properties

Brabender viscoamylograph test, in which the viscosity is plotted against time during a standard cycle of heating with continuous stirring, is a typical method for investigating starch pasting characteristics. Generally speaking, the paste characteristics of starches are mainly affected by the amylose/amylopectin ratio, granule diameter, distribution, and physicochemical properties [39]. The study of pasting properties can tailor functional characteristics to desired applications of starches in traditional industries and also to identify starches with unique characteristics for possible new uses.

Fig. 5 shows the viscosity and temperature profiles of native cassava starch and PPCS with different milling time. The viscosity profile is largely a reflection of the changes in the starch granules that occur during the heating and cooling cycle in the Brabender viscoamylograph. The pasting properties of all these starch samples are given in Table 2. It is seen that all of the characteristic parameters of PPCS, including pasting temperature, peak viscosity, viscosity at 95°C, 95°C-hold, 50°C and 50°C-hold, breakdown and setback, were reduced compared with the native cassava starch. The pasting temperature of native cassava starch was 65.6°C, but decreased to 54.4°C after milled for 30 min, indicating that the PPCS can be easier to cook and requires less heat for gelatinization. This is because the cassava starch granules were destroyed by intensive mechanical actions, allowing greater entry of water into the interior of the granules, which is responsible for the pregelatinization of starch. The pregelatinization of cassava starch in MA process causes the easier gelatinization of PPCS, and thus decreases the pasting temperature of PPCS. Similarly, the peak viscosity and viscosity at different conditions also gradually decreased with increasing the milling time. This may be due to the significant physicochemical property changes of cassava starch under the intensive impact of ball milling, including the breakage of intermolecular and intramolecular hydrogen bonds in

**Table 2.** Pasting properties of native cassava starch and PPCS with different milling time<sup>a)</sup>

Milling time (min)	Pasting temperature (°C)	Peak viscosity (BU)	Viscosity at 95°C (BU)	Viscosity at 95°C-hold (BU)	Viscosity at 50°C (BU)	Viscosity at 50°C-hold (BU)	Breakdown <sup>b)</sup> (BU)	Setback <sup>c)</sup> (BU)
0	65.6 ± 0.3	735 ± 18	451 ± 12	252 ± 5	492 ± 3	458 ± 13	483	240
10	64.2 ± 0.7	668 ± 11	433 ± 6	240 ± 1	467 ± 6	435 ± 9	428	227
20	60.5 ± 0.1	590 ± 3	400 ± 7	215 ± 4	420 ± 11	393 ± 4	375	205
30	54.4 ± 1.2	512 ± 5	352 ± 2	189 ± 6	370 ± 5	349 ± 8	323	181

a) Means of three replicates ± SD.

b) Breakdown = peak viscosity – viscosity at 95°C-hold.

c) Setback = viscosity at 50°C – viscosity at 95°C-hold.

main chains of starch, the rupture of starch molecular chains, the destruction of tight starch granule structure, and the decrease of crystalline phase in starch granules [1, 27, 28]. It shows that the viscosity of cooked PPCS paste decreased as increasing the milling time, but the initial viscosity of PPCS paste in cold water increased with the increase of milling time, which is attributed to the increased degree of gelatinization of PPCS after MA. In wet granulation of drug products, PPCS can be hydrated with cold water to produce viscous slurries or, alternately, can be added directly to the granulator bowl and cold water can be utilized to granulate, which may greatly improve production efficiency. Moreover, the PPCS with lower gelatinization temperature would exhibit better processability and toughness [40].

Compared with the native cassava starch, the breakdown of 30 min milled starch sample reduced from 483 to 323 BU (Brabender unit), and the native cassava starch had the greatest breakdown among all the samples. The breakdown illustrates the stability of the paste during cooking, and lower breakdown implies better stable viscosity with respect to time at high temperature [39]. It indicates that the PPCS was more shearing and thermally stable than native cassava starch. The viscosity after cooling the paste to 50°C reflects the retrogradation tendency or setback viscosity of the cooked pastes [33]. Similar to the breakdown, the setback of 30 min milled sample exhibited an obvious drop compared to that of the unmilled sample, and the native cassava starch also had the greatest setback among all the samples. This may be ascribed to high degree of association of native cassava starch molecules caused by the strong tendency for hydrogen bond formation between hydrogen groups on adjacent starch molecules. When suffered from strong mechanical actions during MA, hydrogen bonds on adjacent starch molecules were weakened and the starch molecules were degraded, contributing to a lower setback of PPCS [1]. When used as excipient in pharmacy, the breakdown and setback of PPCS may affect the rigidity and stability of tablets, and the tablets prepared using the PPCS with lower breakdown and setback can have better rigidity and stability.

#### 4 Conclusions

This study inspected a new method for the preparation of PPCS by MA using a customized stirring ball mill. The measurement of cold-water solubility of different cassava starch samples showed that MA could prepare the PPCS with different degree of gelatinization by controlling the milling time. The characterization using XRD, particle size analyzer, SEM, powder comprehensive characteristics tester, and Brabender viscoamylograph demonstrated that

MA could significantly destroy the crystal structure of starch granules, contributing to the increase of cold-water solubility, flowability, and floodability, the variations of particle size and surface morphology, and the decrease in pasting temperature, viscosity of cooked PPCS paste, breakdown and setback. With these unique properties induced by MA, PPCS was expected to be used as excipient in pharmaceutical formulations as it could exhibit dual functionality as both binder and disintegrant, and improve the production efficiency and qualities of solid oral drugs.

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