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Morphological properties and thermoanalysis of micronized cassava starch

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ABSTRACT

The granule morphology, microstructure, and thermal properties of micronized cassava starch prepared by a vacuum ball-grinding machine were investigated. Scanning electron microscopy (SEM) analysis indicated that the morphology of starch granule changes during the ball-grinding treatment. Differential scanning calorimetry (DSC) analysis indicated that the maximum peak temperature (T_p) of the gelatinization process, the glass transition (T_g), and peak height index (PHI) for the starch granules decreased when the size of micronized starch granules was reduced. When the size of starch granules was reduced beyond 9.11 μm, they have a tendency to agglomerate and their ΔH were increased. The granule size has a significant effect on the gelatinization properties of cassava starch. This study will provide useful information of the micronized starch for its potential industrial application.

1. Introduction

Starch, a major plant source, is widely used in paper, textile, adhesive, and food industries (Che, Li, Wang, Chen, & Mao, 2007a; Jyothi, Sasikiran, Sajeev, Revamma, & Moorthy, 2005; Morikawa & Nishinari, 2000; Pareta & Edirisinghe, 2006; Roberts & Cameron, 2002). Micronized starch made by a vacuum ball-grinding machine belongs to physically modified starch. In the process of micronization, starch granules flake off layer by layer from their surface edge to the interior, ultimately break into anomalous, small granules by means of forces between grinding balls and starch granules, starch granules alone, as well as grinding balls alone. The size of starch granules become small gradually and the starch granule size distribution and the shape of them also change (Edwards, Osborne, & Henry, 2008; Park, Wilson, Chung, & Seib, 2004; Shinji, Makoto, Katsunori, Takuo, & Tetsuya, 1998). From observed changes on the thermal properties of micronized starches during the gelatinization process, we may presume that microstructural changes occur in micronized starches. The micronized starch has a usual application as additives and modifying agent in food industries because of its great specific surface area and reaction activity.

There are two different crystalline structures in the starch system: (i) chain–chain crystal structure between starch molecules formed by hydrogen bond, and (ii) chain–water crystal structure between starch molecule and water molecule formed by hydrogen bond (Lin, Lu, & Liang, 1998). When starch granules are dispersed in water and subsequently heated, three obvious endothermic process along with temperature increase may be observed: (i) starch gelatinization, transiting from crystalline state to amorphous phase, (ii) water volatilization in starch, and (iii) melting of starch chain–chain crystal structure at high temperature, after which starch cooking takes place, also named thermal decomposition process (Donovan & Mapes, 1998). DSC method can be utilized to monitor thermal events occurring during starch gelatinization (Mechteldis & Cone, 1992; Zaidul et al., 2008).

This paper uses vacuum ball-grinding machine to generate MCAST with different granular sizes. The objective of this study is to find the influence of granular size on the morphological and thermal properties of the micronized starch by utilizing SEM and DSC techniques.

2. Materials and methods

2.1. Material and reagent

A commercial cassava starch was purchased from Beijing Quanfeng Starch Company, China. The moisture content of the starch was determined by drying three replicated samples in an air-oven at 105 °C to constant weight (Che et al., 2007b). The average moisture content of the cassava starch was determined as 9.3% (w/w). An analytical grade anhydrous alcohol (95%, w/w) was obtained from Beijing Beihua Chemical Company.

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Nomenclature

d_{10}	the equivalent diameter where 10 vol.% of the particles has a smaller diameter, and the remaining 90% is coarser, μm
d_{50}	the median particle size, μm
d_{90}	the equivalent diameter where 90 vol.% of the particles has a smaller diameter, and the remaining 10% is coarser, μm
$D_{3,2}$	surface weighted mean particle size, μm
$D_{4,3}$	volume weighted mean particle size, μm
DSC	differential scanning calorimetry
MCAST	micronized cassava starch
$MCAST_{6h}$	micronized cassava starch with a micronization time of 6 h
$MCAST_{18h}$	micronized cassava starch with a micronization time of 18 h
$MCAST_{30h}$	micronized cassava starch with a micronization time of 30 h
$MCAST_{42h}$	micronized cassava starch with a micronization time of 42 h
$MCAST_{54h}$	micronized cassava starch with a micronization time of 54 h
PHI	the peak height index, PHI = $\Delta H/(T_p - T_o)$, J/g °C
R	gelatinization range, $R = 2 \times (T_p - T_o)$, °C
SEM	scanning electron microscopy
T	temperature, °C
T_o	onset temperature, °C
T_p	maximum peak temperature, °C
T_c	conclusion temperature, °C
T_g	glass transition temperature, °C
t	processing time, s
Φ	diameter of the grinding ball, mm
ΔH	enthalpy of gelatinization, J/g

2.2. Preparation of MCAST with various granular sizes

A Vacuum Ball-Grinding Machine (QM-1SP04, Nanjing University instrument factory, China) was used for the preparation of MCAST samples. Thirty-six grams of dried cassava starch was dissolved in 80 mL anhydrous alcohol. The suspension was then divided into four sub-samples and placed in four vacuum cans of the ball-grinding machine. Fourteen stainless steel balls ($4 \times \Phi 10$ mm and $10 \times \Phi 6$ mm) were placed in each can. The cans were degassed to lower the inner pressure down to 0.05 MPa. The grinding operation was done for 6, 18, 30, 42, and 54 h at 500 rpm in order to obtain MCAST samples with different granule sizes (Che et al., 2007a; Ren, Mao, Li, & Sun, 2005).

2.3. Particle size analysis

The granule size distribution of starch samples was determined using a particle size analyzer (Mastersizer 2000, Malvern Co., UK) based on laser diffraction method. Anhydrous alcohol was used as the dispersion medium, at 23 °C.

2.4. Morphological properties

The micrographic appearances of the MCAST samples were observed by SEM (S-4300, HITACHI Co., Japan). The starch samples were suspended in anhydrous alcohol to obtain a 1% suspension. One drop of the MCAST-anhydrous alcohol suspension was applied on a glass slide. After the volatilization of alcohol from the suspension, the starch samples were coated with gold to avoid charging under the electron. The thickness of Au-coatings was about 120 Å. An accelerating potential of 15 kV was used during micrography except 1 kV for native starch.

2.5. Thermal properties

A DSC (Q-10, TA Instrument Company, USA) was used to analyze thermal characteristics of micronized starch samples. 2.5 mg starch sample was put into a aluminum pan, and then 7.5 μL distilled water was added, and immediately the mixture was covered with a matched aluminum cover. After equilibrating the samples at room temperature for 1 h, the samples were heated from 30 to 110 °C at the rate of 10 °C/min. For each sample triplicate measurements were taken. Universal Analysis 2000 Data Analysis Software of TA Instruments was used to calculate T_o, T_p, T_c, and ΔH, as well as R and PHI on the DSC curves (Krueger, Knutson, Inglett, & Walker, 1987; Wang et al., 2007; Wootton & Bamunuarchchi, 1979).

2.6. Statistical analysis

The analysis of variance was carried out based on the experimental data by using the SAS statistical package (version 9.0) and p values were used to determine the extent of effect on the properties of MCAST.

3. Results and discussion

3.1. Particle size distribution of MCAST granules

The laser diffraction instrument for particle size measurement provides derived outputs of a volume distribution, standard mean diameters and distribution information (d_{10}, d_{50}, and d_{90}) by assuming spherical particles. d_{10}, d_{50}, and d_{90} are the sizes at which 10%, 50%, and 90% of particles by volume are smaller, respectively. Two most used means are the volume weighted mean diameter (*De Brouckere* mean diameter, $D_{4,3}$) and the surface area weighted mean diameter (*Sauter* mean diameter, $D_{3,2}$). Span, which is defined as $(d_{90} - d_{10})/d_{50}$, is the measurement of the width of the size distribution. The narrower the distribution, the smaller the span becomes (Malvern Instruments, 1999).

The d_{50}, $D_{4,3}$, and $D_{3,2}$ value of micronized starch was reduced from 24.01 to 7.94 μm, 28.38 to 8.54 μm, and 10.73 to 6.12 μm, respectively, with the milling time from 0 to 54 h. Such results were in agreement with Che et al. (2007a) that the granule size was decreased with the increase of grinding time. The influence of milling time on the particle size information of the MCAST granules is illustrated in Fig. 1. As can be seen from Fig. 1, the particle sizes of the MCAST granules was reduced significantly when they were subjected to 6 h of milling time. When the milling time was increased beyond 6 h, the particle size of the MCAST granules was reduced, however, the size reduction of the MCAST granules was not significant when the milling time was higher then 6 h ($p < 0.05$). The span value of the native starch sample was higher than the MCAST samples, suggesting that the particle size distributions of the MCAST samples became narrower compared to that of the native starch sample.

In the initial 6 h of micronization, the inner energy of starch granule increased under the action of mechanical impact. The stress wave appeared at the inside of granule at first, and than

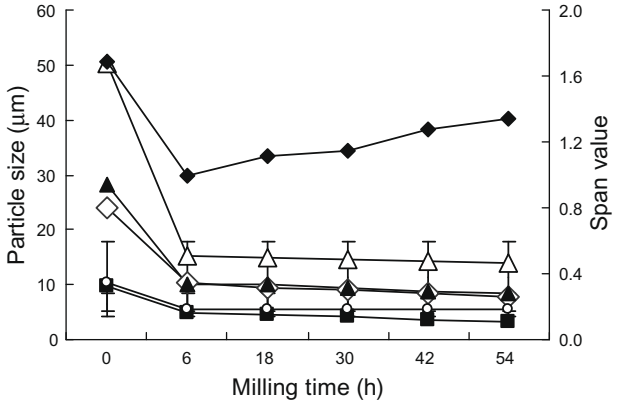

Fig. 1. The influence of the milling time on the particle size information of the MCAST samples: d_{10} (-■-), d_{50} (-◇-), d_{90} (-△-), $D_{4,3}$ (-▲-), $D_{3,2}$ (-○-), and span value (-♦-).

spreaded around, consequently the stress concentration appeared at the disfigurements, cracks and crystal areas, which made granules broke up from these flimsy surfaces. Therefore, it was easy to get smaller granule in the initial 6 h. When the milling time was increased beyond 6 h, the disfigurements inside of granule decreased, and the fragmentation depended on destroying the structure of crystal lattice and made the adjacent molecule chain parted. At this condition, the starch was more difficult to be broken up than the former. As a result, the trend of micronization became slower in the later period, while the particle size was better-proportioned than the initial period, and its distributions became narrower than native starch sample.

3.2. Morphological properties of MCAST

Fig. 2 shows the SEM pictures of MCAST. The morphological characteristics of cassava starch changed markedly after the micronization process. The granule surface of native cassava starch was smooth, had no convex–concave phenomenon, and half of single granule presented rotundity and truncation rotundity. With the increasing of milling time, the granule surface of starch formed cracks, and some of fragments fell off from granule surface, so that the surface of starch granules changed from slick to rough. In addition, the rupture and fragmentation appeared in the bigger granules, and then most of the starch granules parted to smaller fragments. More granules were impacted to flat shape in the action of force and cracked to flakes from edges, as a result, a large number of smaller and irregular fragments were created (Shinji et al., 1998). The conglomeration of the MCAST granules was evident after vacuum ball-grinding treatment for 54 h.

As can be seen from Figs. 2 and 3, the decrease of the starch granules size was not only from the surface layer step by step, but lots of thicker layers desquamate around the granule, and many layers broke down from the core during the process of the vacuum ball-grinding treatment.

3.3. Thermoanalysis of MCAST

Fig. 4 shows DSC curves of MCAST of different granularities. Thermal properties of MCAST granules are summarized in Table 1. As can be seen from Fig. 4, there are two obvious endothermal peaks exist at the range from 30 to 110 °C. The first endothermic peak at low temperature is caused by the gelatinization of polycrystalline state in native starch, for the reason that double phase transition occur from polycrystalline state to amorphous phase. The other peak at about 100 °C is caused by volatilization of water in MCAST samples.

Water content of starch samples can significantly influence thermal properties, for example, the glass transition (T_g) of starch samples would decrease along with water content increase since water in starch acts as plasticizing agent and its movement would have great influence on the mass and structure changes of starch containing product (Akinori, Masata, & Masao, 1998). The DSC

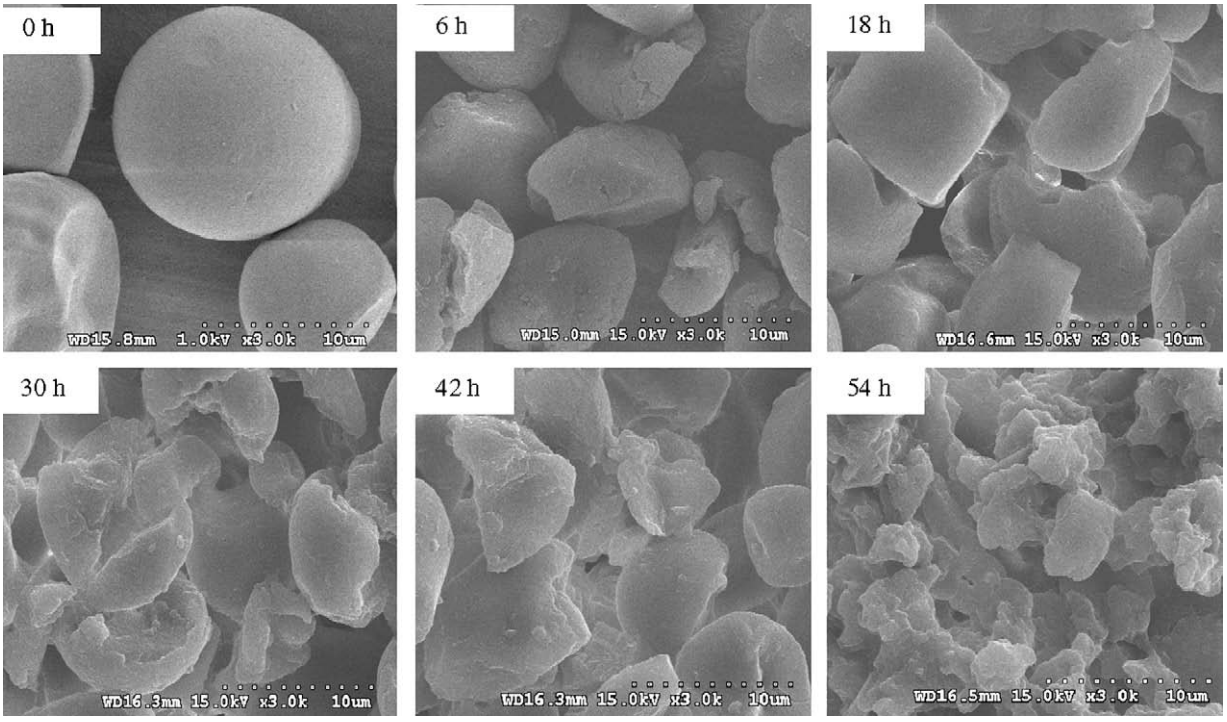

Fig. 2. SEM micrographs of different MCAST samples after vacuum ball-grinding.

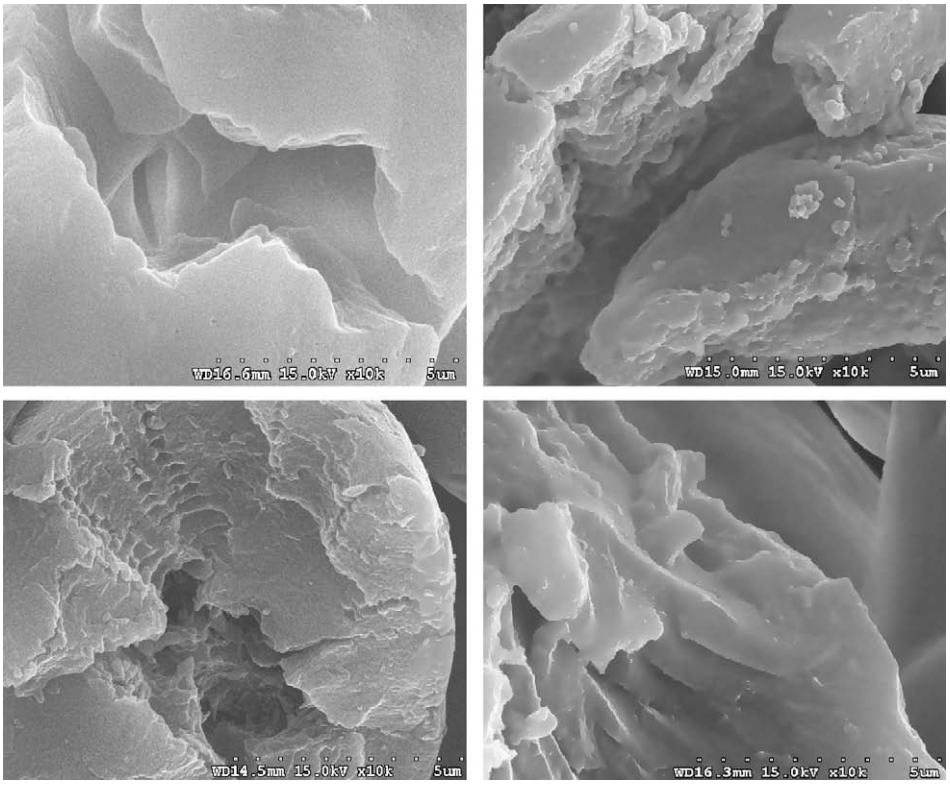

Fig. 3. SEM micrographs of MCAST samples: layers broken down from the core during the process of the micronized treatment.

curves of native cassava starch (d_{50} = 24.01 μm), MCAST (6 h, d_{50} = 10.24 μm) and MCAST (18 h, d_{50} = 9.31 μm) show step changes in the heat flow signal besides the gelatinization (endothermic) peak, suggesting that glass transition occurs for these starch samples. The T_g of native cassava starch, MCAST (6 h) and MCAST (18 h) were determined as 52.98 °C, 50.48 °C, and 48.18 °C, respectively. The T_g of the MCAST samples was reduced with the increasing of micronization time. Even though the glass transition temperature of the MCAST (18 h) sample dropped slightly (from 52.98 to 48.18 °C) compared with native starch sample, the ΔH of the MCAST (18 h) sample dropped sharply from 5.53 to 0.4838 J/g. However, when the micronization time was in-

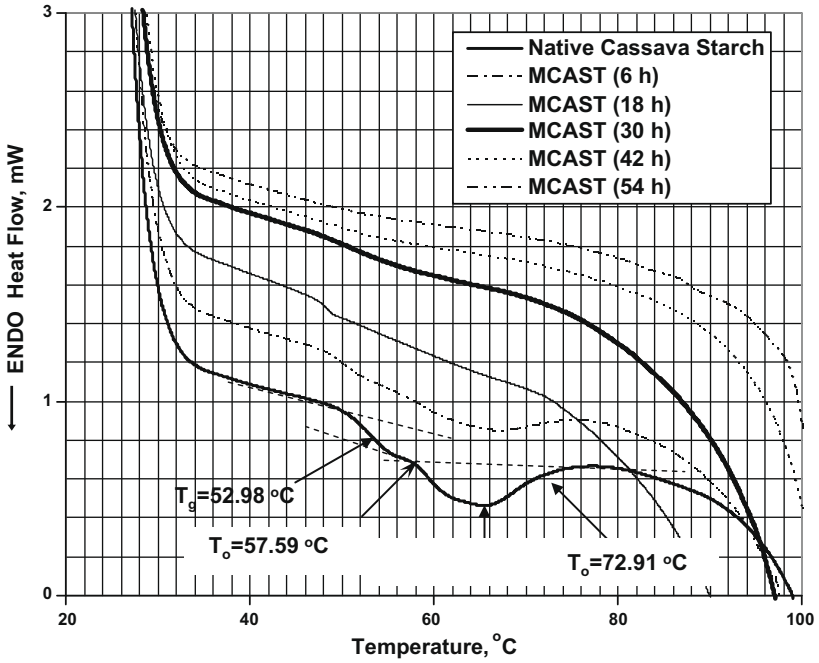

Fig. 4. DSC curves of the MCAST samples.

Table 1
Thermal properties of MCAST.

Sample	T_o/°C	T_p/°C	T_c/°C	T_g/°C	ΔH/J/g	R/°C	PHI/J/g °C
Native starch	57.59 (1.28)	65.34 (1.33)	72.91 (2.01)	52.98 (1.81)	5.53 (0.22)	15.5	0.71
$MCAST_{6h}$	54.95 (1.44)	64.97 (1.51)	72.75 (1.88)	50.48 (1.66)	3.930 (0.14)	20.04	0.39
$MCAST_{18h}$	49.65 (1.06)	62.36 (1.62)	71.43 (1.79)	48.18 (1.34)	0.4838 (0.04)	25.42	0.38
$MCAST_{30h}$	48.13 (1.13)	56.30 (1.54)	60.92 (1.80)	–	0.8696 (0.07)	16.34	0.106
$MCAST_{42h}$	46.11 (0.97)	55.58 (1.22)	55.92 (1.39)	–	0.9457 (0.06)	18.94	0.0998
$MCAST_{54h}$	41.73 (0.92)	52.18 (1.05)	55.11 (1.21)	–	1.036 (0.08)	20.0	0.0991

Standard deviation in parentheses.

creased beyond 18 h, no significant change was observed in the values of ΔH. This observation suggests that the micronization process has a great influence on the thermal properties of the MCAST starch samples. Similar results were observed for wheat starch samples studied by Eliasson and Karlsson (1983) and Evers and Stevens (1985) using DSC technique. Compared with native starch sample, T_o, T_p, and T_c of the MCAST starch samples were reduced with the decreasing of the size of the MCAST granules.

In fact, the structure change of the micronized starch granule had a great influence on the characteristic and behavior of starch during thermal process. After micronization, the crystal lattice of starch was broken, disordering degree increased, crystalline degree and melt temperature declined. Therefore, in contrast of native starch, the micronized starch granule absorbed less water and was easy to be gelatinized under thermal treatment due to the polymer chains became weak or broken. Normally, the glass transition referred as phase of amorphous transfer to the state of crystalline. The amount of available water in the system would be increased when the size of starch granule was reduced, and led to the decrease of the glass transition temperature.

4. Conclusions

The size of the native cassava starch would reduce and the morphological character changes evidently along with vacuum ball-grinding time increase during micronization.

DSC curves of MCAST show that gelatinization endothermal peak of each MCAST tend to level off, their gelatinization T_o, T_p, and the T_c tend to decrease with the reducing of the granular size. Under the experiment condition, when the $d_{50} \geqslant 9.31$ μm, glass transition occurs, moreover, the T_g, ΔH and PHI all decreased along with the reducing of the granular size.

The conglomeration of the MCAST granules becomes powerful when the $d_{50} \leqslant 9.11$ μm, which brought the higher ΔH, but their PHI are similar.

The research illustrates starch gelatinization process do not go along at the same time, but from the surface to center of granules, ultimately the whole granule is gelatinized thoroughly. Thermal characters of micronized starch change to some extent as well.

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