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# Influence of ultra-fine friction grinding on microstructured Sago starch particles and suspension films

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**Abstract.** Microstructured sago (*Metroxylon sagu*) possesses an excellent potential to be used for numerous applications. In this paper, sago starch microparticles (SMPs) were fabricated using an ultra-fine grinder without any chemical treatments or purification steps thus making it a "green" and an eco-friendly procedure. The effects on increasing the numbers of passages through the grinder on the resulting SMPs and as suspension films were investigated. We observed that after 7 cycles the average diameter was reduced to a microscale region of 0.811 ± 0.754 μm (811 nm). The highest tensile strength was shown to be the highest after 3 cycles of 2.308 ± 0.210 MPa and repeated cycles beyond 7-cycled SMPs process had resulted in damaged microparticles. Furthermore, water vapor permeability was observed in SMPs with higher number of grinding cycles, with 7-cycled SMPs being 15.522 ± 0.184 g mm/m$^2$ h Pa and 10-cycled SMPs, 19.763± 0.233 g mm/m$^2$ h Pa. Our results demonstrated that the final particle size, water vapor permeability and tensile strength of the SMPs suspensions films were affected by the number of passages through the mechanical grinder.

## Introduction

After cellulose, starch is the second most abundant carbohydrate in nature [1]. Due to their abundance, cost-saving, biocompatibility and renewability, starch and its derivatives have emerged as important biomaterials that can be exploited for various applications, most notably in biomedical and industrial sectors. Some of the promising applications are as drug carriers [2], biodegradable packaging materials [3] and fat replacers in food materials [4]. Microparticles have also wide applications in novel food products development since structural changes to micro-size levels can affect physicochemical and sensory properties qualities of food thus improving the quality of processed foods.

Several methods to fabricate starch microparticles have been explained in the literature by adipic acid-modified dry preparation technique, aqueous-alcoholic treatment, molecular rearrangement of short-chain glucans, rapid ultrasound, electrostatic spray and supercritical $CO_2$, premix membrane emulsification, reactive extrusion, inverse crosslinking-emulsion method and alcohol–alkaline treatment. However, these methods involve chemicals treatments or addition of chemical reagents and purification steps to obtain a final product, which could be undesirable for certain applications. In this study, a "green" process was employed to obtain microparticles of sago starch. The process involved with an ultra-fine friction grinder or known as "super mass colloider (SMC)" without using any chemical treatments or reagents. The ultra-fine particles obtained *via* this method permits the use of concentrated suspensions without prior filtration [5].

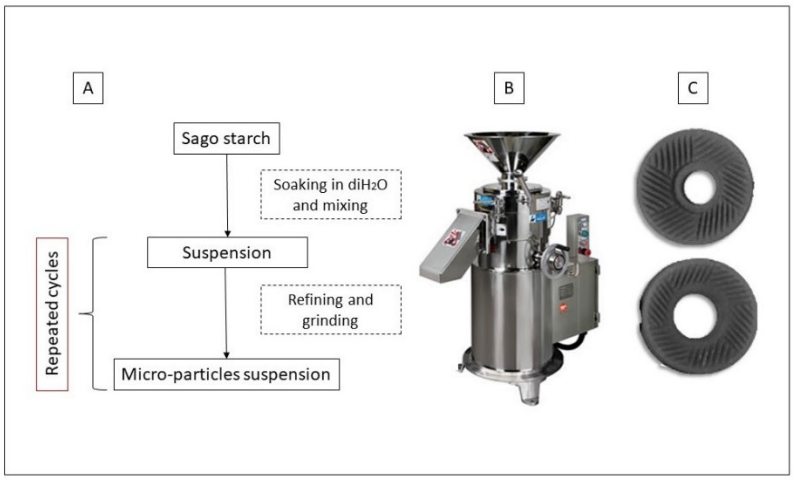


*Figure 1. (a) Schematic flow of sago starch microparticles fabrication; (b) Super Masscolloider (Masuko Sangyo, Saitama, Japan); (c) grinding stones.*

As seen in Figure 1(c), SMC comprises of two grinding discs or rotary grinder with a grove design to ensure an accurate flow of the feed toward the grinding area. The gap distance amongst the two discs can be modified vertically by displacing the rotary disc in 1/100 mm increment. Furthermore, higher compression, shearing, and rolling friction forces can be achieved by employing a smaller gap resulting in closer contact of rotary grinders. The ceramic and non-porous grinding stones avoid bacterial growth and cracks linked with thermal stress that can be normally found in conventional grinding. The energy consumption of this technique is also comparable with homogenization and micro-fluidization [7]. Conversely, the particle size acquired after ultra-fine grinding is larger than that obtained after other methods such as high-pressure homogenization. Various sources have been described and reported in literature using this technique to obtain micro- and nano materials. Such sources include cellulose, jute fibers, date palm, carrotsbamboo fibres, turmeric and sugar palm.

Sago (*Metroxylon sagu*) palm is a type of starch native to South East Asia [8] with its stem possesses the highest starch content as compares with maize, rice and cassava [9]. Sago palm is known to be exceptionally resistant to unfavourable weather environments portraying its important part in food security issues. The chemical and physical characteristics of sago starch as a biomaterial, however, was less known to researchers in the past. Consequently, there have been a recent rise in scientific and commercial interest in the investigation and development of sago starch particularly modifications in chemical and physical structure, molecular structure, physicochemical and functional properties [9]. At present, research in sago starch potential is still in its infancy compared to its starch counterparts.

## Experimental

*Materials*

Only sago starch powder - acquired from NZA Enterprise, a local sago production company in Brunei Darussalam and deionized water were used to produce sago micro-particles (SMPs) in this work.

*Fabrication of micro-particles*

Figure 1 shows the production steps of SMPs. Sago starch (2 wt. %) powder were mixed with deionized water and stirred for 2 days in room temperature. The sago homogenates were processed using SMC (Masuko Sangyo, Saitama, Japan) that consists of two grinding stones that rotates at a high speed. Procedures were repeated 10 times to obtain SMPs in smaller sizes and samples

produced were denoted based on their cycles as x-SMPs, whereby, each batch of grinding was counted as one pass.

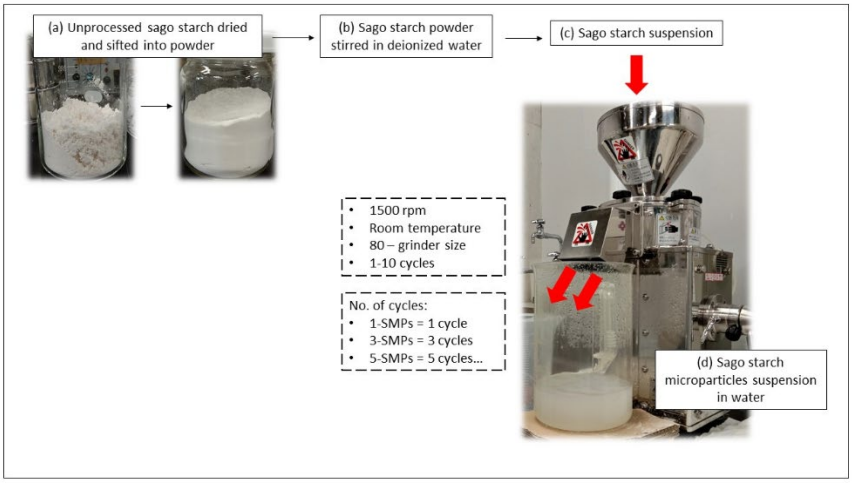


*Figure 2. Stages of sago-microparticles production using ultra-fine grinder machine.*

*Preparation of sago micro-particles suspension films*

Films of the sago suspensions after every cycle were prepared using solvent casting method in which 40 mL aliquots of the suspension were poured onto teflon plates and placed in an oven (Eyela Vacuum Oven, VDS-201SD) at 30 ± 1 °C for 15 hours. Prior to any testing, the film specimens were preconditioned in a climate chamber at 25 °C and 50% RH for at least 48 hours.

Micro-particles analysis

*Scanning electron microscopy*

The particles microstructure and fracture surfaces were observed a scanning electron microscope (SEM) instrument (SU3500, Hitachi, Tokyo, Japan). A drop of undiluted microparticles suspension was deposited on a glass plate attached on metal stubs, formerly covered with double sided adhesive. All specimens were sputter-coated with gold using Eiko Sputter Coater under vacuum condition.

Particle size determination

Dynamic light scattering method was performed using particle size analyzer device (ELSZ-2000 Series, Otsuka Electronics, Japan) to determine the distribution of particles. The undiluted microparticles dispersions were sonicated prior to the measurement and immediately measured to prevent sample precipitation.

*Characterization of SMPs suspension films*

*Thickness, water solubility and swelling kinetics*

The thickness of suspension films was carried out using a digital micrometer (Mitutoyo, Japan) with an accuracy of ±0.001 mm. The reported results were the mean value of ten measurements for each sample expressed in millimeters (mm).

Total water solubility of SMPs suspension films were defined as the weight of dissolved film after being immersed in distilled water. Film specimens (20 mm by 20 mm) were prepared dried at 100 ± 2°C for 24 hours in a laboratory oven and weighed to determine the initial dry mass. Film specimens were then immersed in performed in 50 mL of distilled water for five hours with

constant agitation. The resultant pieces of films were taken out, filtered and dried at 100 ± 2°C for 24 hours.

Prior to determining the swelling kinetics of SMPs suspension films, the specimens were prepared by cutting into 10 mm by 10 mm squares and dried in an oven at 60ºC for 24 hours. The dried film specimens were immersed in beakers containing distilled water and weighed for every 2 hours. The test was carried out in triplicates and the swelling ratio (SR) was calculated by the following equation:

$$SR\ (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where $W_s$ and $W_d$ are the swollen and dry weight of films at time t, respectively.

*Water vapor permeability*

Prior to water vapor permeability (WVP) analysis, the films were first conditioned in a desiccator at 25 °C for 48 hours. SMPs suspension films were cut in circular shape about 30 mm in diameter and positioned over the test cup, which was prefilled with anhydrous calcium chloride, leaving 5 mm to the top. The suspension films were then fastened with melted paraffin. The assembly was placed in a chamber conditioned at 25 °C and 100% RH and weight increments of the cup were measured and plotted at intervals. The WVP was calculated as follows:

$$WVP = \frac{m \times d}{(A \times t \times P)} \quad (2)$$

where d is the thickness of films (m), m is the weight increment of the cup (g), A is the area exposed ($m^2$), t is the permeation time (h), and P is the difference in partial pressure of water vapor across the film (Pa). All specimens were tested in triplicates.

*Tensile test*

Film specimens were cut into dumbbell shape strips and dried in oven at 50 °C prior to the investigation to eliminate any leftover moisture. The samples were stretched at 0.500 mm/s with 100 N load. Tensile strength (MPa), Young's Modulus (MPa) and elongation at break (%) were assessed using Universal Testing Machine (EZ Graph, Shimadzu, Kyoto, Japan).

*Statistical analysis*

All data in this study were expressed as means ± standard deviations of triplicates. Statistical significance of differences between mean values was assigned by one-way ANOVA with Tukey's test at a confidence level of $P < 0.05$ using OriginPro software (OriginLab Corporation, USA).

## Results and discussion

*Morphological and Mechanical studies of SMPs*

The surface morphology of microparticles in Figure 3 shows that increased number of cycles produced particles of finer sizes. Clear differences can be seen in Fig. 3(a), whereby 0-SMPs exhibited an average diameter of 25.140 ± 1.853 μm. Minimal polydispersed microparticles were also obtained by ultra-fine grinder after 7 cycles where average diameter was reduced further to a microscale region of 0.811 ± 0.754 μm (811 nm) in Fig. 3(b).

An increment in grinding cycles of SMPs had resulted in lower tensile strength, Young's modulus as well as elongation at break ($P < 0.05$). The highest tensile strength was observed in 3-SMPs of 2.308 ± 0.210 MPa and it gradually decreases with increasing grinding cycles.

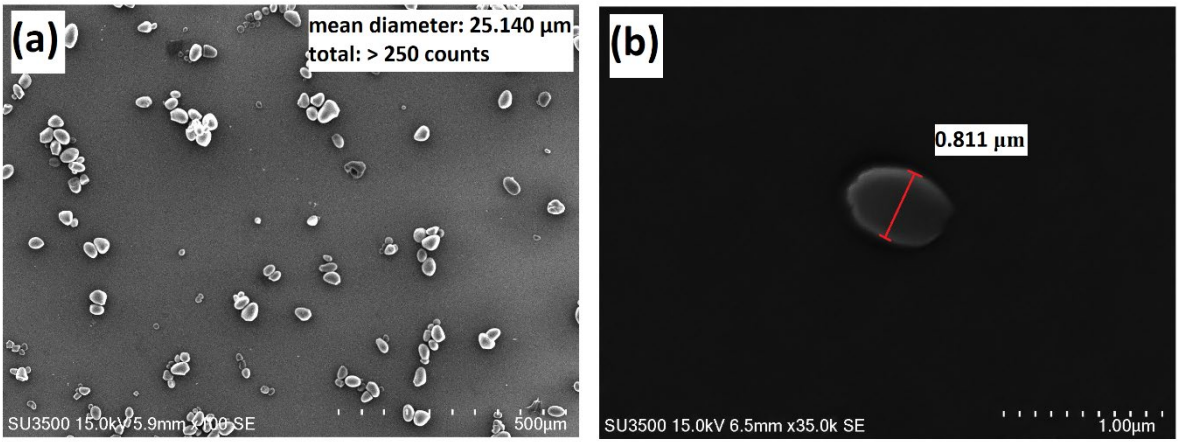


*Figure 3. SEM images of (a) sago starch at 0 cycle at x100 and (b) single sago micro-particle after 7 cycles at x35.0k.*

Consequently, repeated cycles beyond 7-SMPs process had resulted in damaged microparticles as shown in Fig 4.

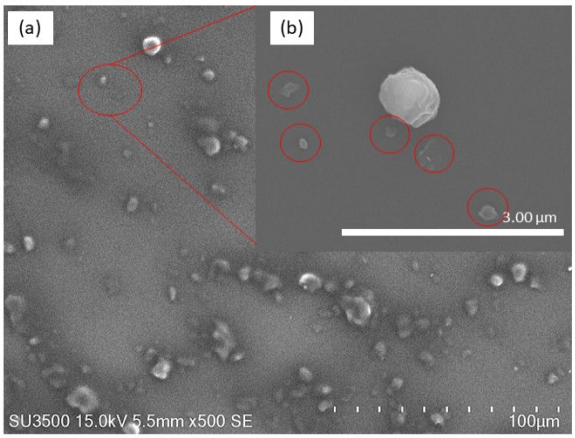


*Figure 4. (a) Destroyed SMPs after 10 complete cycles. (b) Breakdown of smaller particles from a single microparticles.*

*Particle size distribution*

The result by dynamic light scattering exhibited a slightly broad particle size distribution with the highest intensity of micro-particles recorded at 11.338% for 811.561 µm.

Physical properties of SMPs suspension films

Thickness of suspension films ranged between 0.087 mm to 0.093 mm and there were no significant differences detected in these film suspensions. In terms of total solubility in water after 24 hours immersion, it can be deduced that water solubility was significantly higher after 10 passages. Increasing the grinding cycles had caused the suspension films to become more susceptible to water uptake and retention. The increase in water vapor permeability was observed

in SMPs with higher number of grinding cycles, with 7-SMPs being 15.522 ± 0.184 g mm/$m^2$ h Pa and 10-SMPs, 19.763± 0.233 g mm/$m^2$ h Pa.

## Conclusion

This work reports on green fabrication of sago starch microparticles using a rapid, simple, and eco-friendly ultra-fine grinding technique. Repeated cycles had proven to have major drawbacks where the fabricated microparticles were damaged resulting in cracks and fissures and decreased SMPs suspension films total water solubility, water vapor solubility and mechanical properties. Nonetheless, damaged granules still exhibited great potentials to be employed in several applications such as drug carriers in drug delivery systems and food processing especially considering their renewable source, nontoxicity and cost-effectiveness.

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