

Physico-chemical and Thermal Properties of Starch Derived from Sugar Palm Tree (*Arenga pinnata*)

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Received: 18 April 2013;

Accepted: 27 August 2013;

Published online: 15 February 2014;

AJC-14677

Petroleum based polymers are extremely stable and commonly used in various industries include food packaging, furniture and automotive. However, the waste that come from petroleum based polymer material has brought negative impact not only for human being, but also create the serious environmental problems. Hence, biopolymers that come from natural source such as starches are now being considered as an alternative to the existing petrochemical based polymers. This study was aimed to examine the potential of sugar palm starch extracted from sugar palm tree (*Arenga pinnata*) as a new biopolymer. The important properties of sugar palm starch studied were the chemical properties, thermal properties, particle size and morphological surface. The starches isolated from sugar palm tree contained comparable amounts of amylose (37.60 %) which were higher than tapioca, sago, potato, wheat and maize. The results showed significant differences in the chemical content as well as in the granule sizes of sugar palm starch. Thermal characteristic studies using thermogravimetry analysis and differential scanning calorimetry showed that sugar palm starch was thermally stable than other starches. Study on morphological surface indicated that sugar palm starch were rounded and oval-shaped.

Keywords: Sugar palm starch, Biopolymer, Chemical properties, Thermal properties.

INTRODUCTION

Sugar palm tree is one of multipurpose trees grown in Malaysia. It is a member of the *Palmae* family and naturally a forest species. It belongs to the subfamily *Arecoideae* and tribe *Caryoteae*. Haris¹ reported that sugar palm have approximately around 150 local names indicating its multiple uses by the villagers. The names includes, *Arenga pinnata*, Areng palm, Black fibre palm, Gomuti palm, Aren, Irok, Bagot and Kaong. One of the most important products of the sugar palm tree is palm sugar locally known as *neera* sugar. *Neera* sugar usually used as food sweetener in traditional food. Palm sugar can be consumed freshly or let it be fermented for a while to become palm wine². It has been reported that sugar palm was the first sources of sugar, fermented drinks and syrup³.

Besides yielding *neera* sugar, it also provides a great variety of products such as ropes, filters, brooms and roof materials. Sugar palm tree can also produce juices from its fruits. The fruits are white in colours which are taken from its fruit bunch. They can be preserved in heavy syrup for canned

product and the fruits can be cooked with sugary syrup for desserts. The outer part of the stem consists of wood which is extremely hard and durable. It can be processed for flooring, furniture and hand grips of tools. It is also reported that the sugar palm's roots are useful for medicine^{4,5}. Nowadays, researchers are more focusing on production of bioethanol that can be derived from *neera* sugar via fermentation process^{6,7}.

Apart from that, sugar palm starch (SPS) also accumulates in the core of the stem of the sugar palm. The common industrial starches are typically derived from cereals (corn, wheat, rice, sorghum), tubers (potato, sweet potato), roots (cassava) and legumes (mung bean, green pea). Sugar palm starch is the example of starch derived from another source, the stem of sugar palm same as commercial starch extracted from sago palm. It has been documented that one tree of sugar palm can produce 50 to 100 kg of starch⁸.

Due to unique behaviour of starch, many researchers have been using it as biopolymer⁹. Teixeira *et al.*¹⁰ used plasticized cassava starch as a biopolymer and combined it with cassava bagasse cellulose nanofibrils as reinforcing materials.

Prachayawarakorn *et al.*¹¹ prepared biodegradable polymer from thermoplastic rice starch (TPRS). Vallejos *et al.*¹² applied corn and cassava starches plasticized with 30 wt % glycerin as biopolymer and using fibrous material obtained from ethanol-water fractionation of bagasse as reinforcement. However, up till today, there is no research been carried out to evaluate the potential of sugar palm starch as biopolymer. Hence, this study was done in order to investigate the properties of sugar palm starch and to explore their potential to be used as a new alternative biopolymer.

EXPERIMENTAL

Extraction of sugar palm starch: The sugar palm starch (SPS) was collected from sugar palm tree at Jempol, Negeri Sembilan, Malaysia. Fig. 1 shows the extraction method of sugar palm starch. Firstly, the matured sugar palm tree was felled using chainsaw and the mixture (woody fibres and starch powder) was obtained from the interior part of the stem. This mixture was then carried out for washing process to obtain the starch. In washing process, water was added to the mixture and then the mixture was kneaded by hand. The fibers remain on the top of the sieve while the water carrying the starch granules in suspension passes through the sieve and was caught in container. The starch settles on the bottom and the excess water flows over the sides. After washing process, the fibrous remnants were discarded and the wet starch was taken out from the container. Then starch was kept in an open air for a moment and dried in an air circulating oven at 120 °C for 24 h.

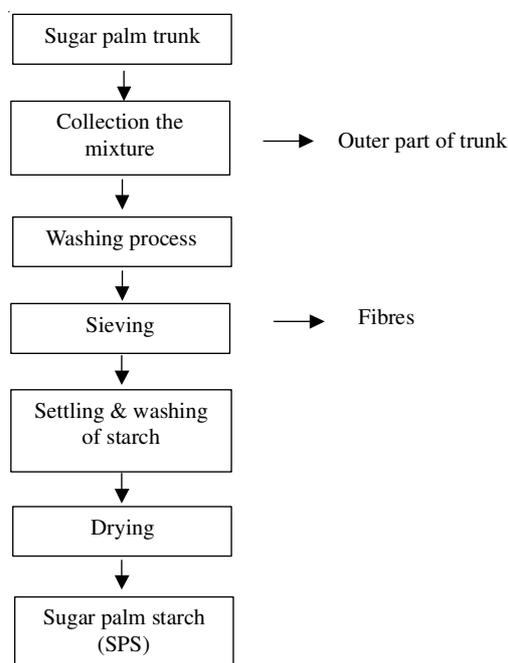


Fig. 1. Extraction of sugar palm starch

Measurement of density: The density (ρ) of sugar palm starch was determined using specific gravity bottle and water as liquid. Initially, sugar palm starch was weighted (m) and then immersed into water. The amount of water before and after immersion was recorded as the volume (V) and was used in the determination of the density of sugar palm starch.

$$\rho = \frac{m}{V}$$

where ρ is the density of fibre, m is the mass of fibre, V is the volume of water.

Determination of amylose: Amylose content of sugar palm starch was determined according to IRRI method¹³ using spectrophotometer.

Determination of ash: An accurately sample (5 g) was weighted and incinerated in a muffle oven at 600 °C until a constant weight was achieved. Ash content was calculated as the weight of the residue divided by the original weight of the sample, expressed as percentage.

Determination of moisture content: Sugar palm starch was weighted using a weighing balance and recorded as M_1 . The samples were dried in the oven at 105 °C for 24 h and reweighted (M_2). The moisture content was calculated using formula shown below:

$$\text{Moisture content (\%)} = \frac{M_1 - M_2}{M_1} \times 100$$

where, M_1 = weight of air dried sample (g), M_2 = weight of oven dried sample (g).

Fourier transform infrared (FT-IR) spectroscopy: The spectra were obtained using an IR spectrometer (100 Series type, Perkin-Elmer). About 2 mg of sample which is in powder form was mixed with potassium bromide (KBr) and pressed into a disc of *ca.* 1 mm thick. The FT-IR spectra of the sample were collected in range of 4000-200 cm^{-1} . FTIR allows the measurements of variations on samples because of the chemical treatments. FTIR of the samples were recorded in the transmittance mode.

Thermogravimetric analysis (TGA): Sugar palm starch was prepared for TG analysis. The thermogravimetric analysis (TGA) conditions were: a nitrogen atmosphere, a flow rate of 20 mL min^{-1} , a heating rate of 10 °C min^{-1} and a temperature range from ambient to 800 °C.

Differential scanning calorimetry (DSC): DSC measurements were carried out in a Shimadzu TA-50WSI Thermal Analyzer equipped with DSC-50 modules. The scans were carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} , using a nitrogen atmosphere with a flow of 20 mL min^{-1} .

Particle size analysis: Particle size and distribution was analysed by using Mastersizer 2000 E (Malvern Instruments, Malvern, UK) fitted with the Qspec Dry powder Feeder.

Scanning electron microscopy (SEM): Scanning electron microscopy (SEM) Hitachi S-3400N operating at an acceleration voltage of 0.3-30 kV was performed to study the surfaces morphology of the native sugar palm starch.

RESULTS AND DISCUSSION

Chemical properties: It is known that sugar palm starch and other commercial native starches contain 10-20 % moisture under normal atmospheric conditions. Since starch is very sensitive to water, the amount of water absorbed by starch granules is dependent on the relative humidity (RH) and the temperature of the atmosphere in which they have been stored. The starches isolated from sugar palm starch contained

comparable amounts of amylose (37.60 %) which were higher than that of tapioca (17 %), sago (24-27 %), potato (20-25 %), wheat (26-27 %) and maize (26-28 %). All kinds of starch contain two types of glucose polymers *i.e.*, an essentially linear molecule termed amylose and a highly branched polymer termed amylopectin. Amylose molecules consist of 200-20,000 glucose units which form a helix as a result of the bond angles between the glucose units. Amylopectin is a highly branched polymer containing short side chains of 30 glucose units attached to every 20-30 glucose units along the chain. Amylopectin molecules may contain up to two million glucose units (Fig. 2). The amylopectin content is calculated from: amylose content + amylopectin content = 100 %.

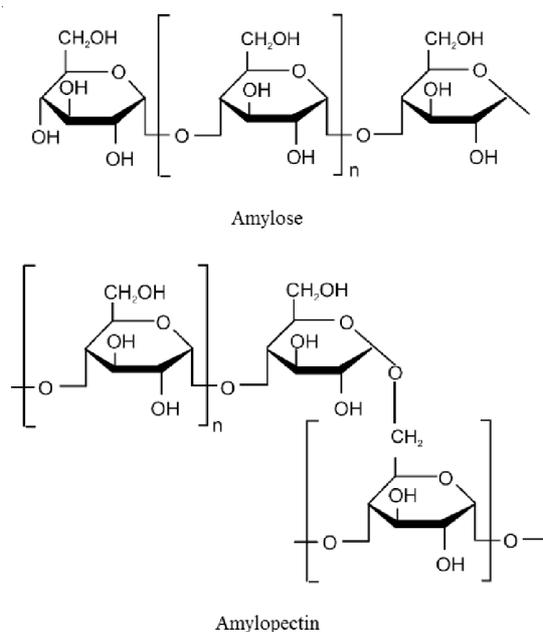


Fig. 2. Unit structure of amylose and amylopectin³¹

Proportion of the polysaccharides amylose and amylopectin become the most critical criteria that determine starch behaviour^{14,15}. Most amylose molecules (molecular weight ~ 105-106 Da) are consisted of (1→4) linked α -D-glucopyranosyl units and formed in linear chain. But, few molecules are branched to some extent by (1→6) α -linkages^{16,17}. Amylose molecules can vary in their molecular weight distribution and in their degree of polymerization (DP) which will affect to their solution viscosity during processing and their retrogradation/recrystallization behaviour, which is important for product performance. Meanwhile, amylopectin is the highly branched polysaccharide component of starch that consists of hundreds of short chains formed of α -D-glucopyranosyl residues with (1→4) linkages. These are interlinked by (1→6)- α -linkages, from 5-6 % of which occur at the branch points. As a result, the amylopectin shows the high molecular weight (107-109 Da) and its intrinsic viscosity is very low because of its extensively branched molecular structure.

For ash contents, sugar palm starch shows 0.2 % ash content same as tapioca, sago and wheat starches. The ash content can be determined as the residue after ignition of the starch at 600 °C. From the table, it is found that potato starch has a relatively high ash-content compared because of the presence

of phosphate groups. As metals, the ash of native starches contains mainly calcium, potassium, magnesium and sodium¹⁸.

FTIR analysis: The FTIR technique detects the absorption of different bond vibrations in starch molecules and it is sensitive to changes in molecular structure such as starch chain conformation, helicity, crystallinity and moisture content. FTIR was used in order to detect the presence of the functional groups existed in sugar palm starch. Fig. 3 shows the FT-IR spectrum of sugar palm starch. The intense peaks at 3500-3200 cm^{-1} shown in figure indicated the presence of O-H groups in sugar palm starch. This prove that starches are very sensitive to water molecule due to the present of hydroxyl groups. Meanwhile, the strong peaks at 3000-2850 cm^{-1} assigned to the C-H stretching and peaks at 1030-990 cm^{-1} was characteristic of the anhydro-glucose ring O-C stretch¹⁹. The peaks at around 1450 and 1200 cm^{-1} were characteristic of C-O-H. While, peaks at 1600-1500 cm^{-1} attributed to the bending of water in starch²⁰.

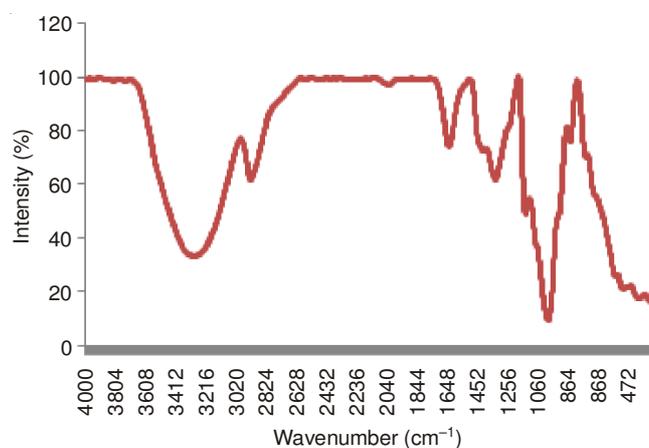


Fig. 3. FT-IR spectrum of sugar palm starch

Thermal properties: Thermogravimetric analysis is one of the thermal analysis techniques used to measure the mass change, thermal decomposition and thermal stability of material. Figs. 4 and 5 demonstrate the TG and DTG curve of sugar palm starch. The molecular structure of sugar palm starch will be degraded when heated. The mass loss below 100 °C may be attributed to evaporation of absorbed moisture²¹. The large degradation at 310 °C appears to involve further elimination of the polyhydroxyl groups, accompanied by depolymerization and decomposition²². It has been documented earlier that at higher temperatures, depolymerization of the macromolecules takes place with the formation of b-(1,6) anhydro D-glucopyranose (levoglucosan), 2-furaldehyde (furfural) and a range of lower molecular-weight volatile and gaseous fragmentation products. A carbonaceous (substance rich in carbon) residue remains after all the volatile products have been driven off²³.

DSC is a thermal analysis technique that measures the temperature and heat flow associated with transition in materials as a function of temperature and time. One of the most widely used applications of DSC is the determination of glass transition (T_g), melting point (T_m) and energy of fusion²⁴⁻²⁷. From the curves in Fig. 6, T_g and T_m of sugar palm starch was around 242.14 and 279.84 °C, respectively. These value were higher than Indica rice starch where T_g values was 237 °C and T_m was 276 °C²⁸. Luiz *et al.*²⁹ have been reported that melting

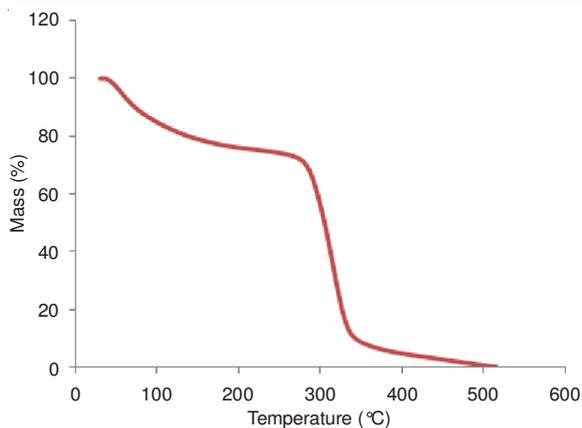


Fig. 4. TG curve of sugar palm starch

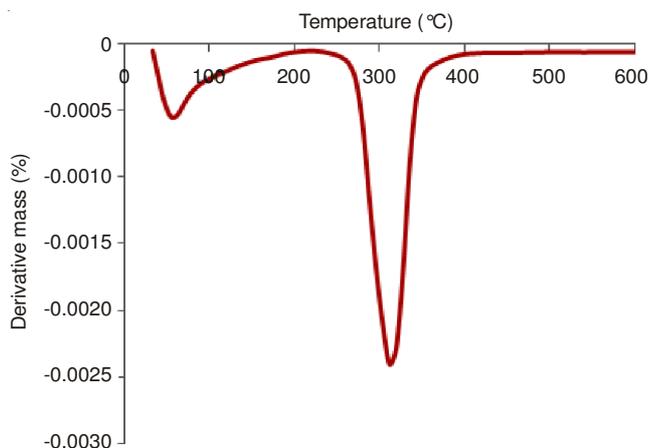


Fig. 5. DTG curve of sugar palm starch

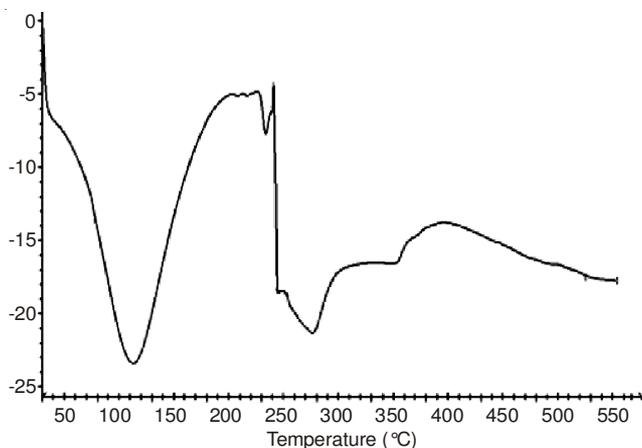


Fig. 6. DSC curve of sugar palm starch

point of cassava starch occurred at 169.2 °C. Thermal characteristic studies using thermogravimetry analysis and differential scanning calorimetry showed that sugar palm starch was thermally stable than other starches.

Particle size: Starches from various sources are chemically similar and their granules are heterogeneous with respect to their size, shape and molecular constituents. Fig. 7a shows the particle size analysis of sugar palm starch. It was revealed that the sugar palm starch had the highest mean diameter (36.308 μm) with a particle size distribution ranging from 0.020-1000 μm. The results observed for the sugar palm starch peak are comparable to the tapioca starch as shown in Fig. 7b.

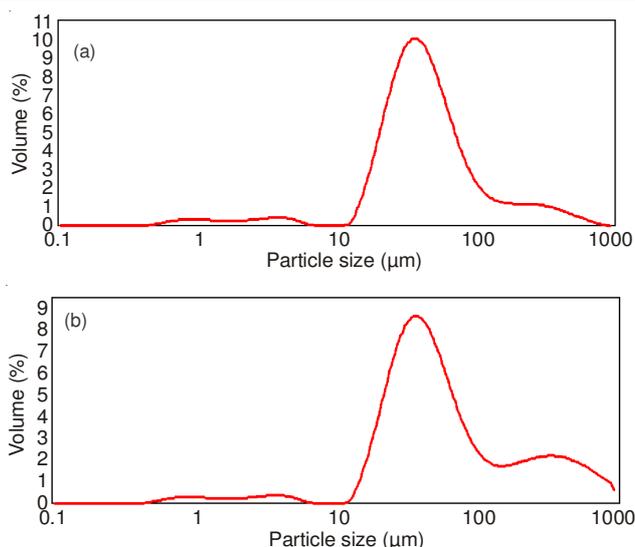


Fig. 7. Particle size distribution of (a) sugar palm starch and (b) tapioca

The particle size of starch is one of the most important characteristics, which may influence other physicochemical properties such as swelling power and water-binding capacity³⁰.

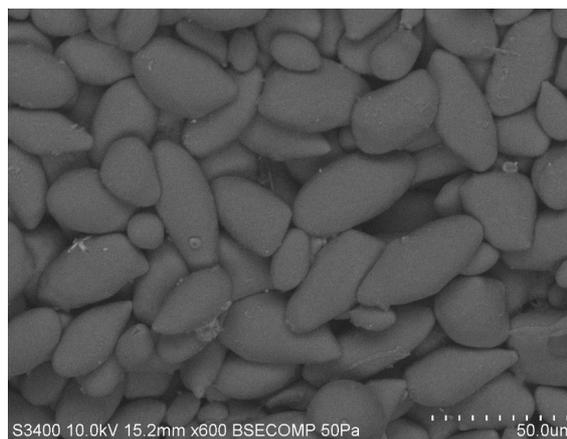


Fig. 8. Scanning electron microscopy of sugar palm starch

Scanning electron micrographs: The scanning electron micrographs of sugar palm starch granules was shown in Fig. 8. The starch granules of sugar palm starch when viewed by SEM were rounded and oval-shaped granules with smooth surfaces. From the micrographs, it is estimated that the granule size ranges from approximately 10-100 μm, which is in agreement with the study on particle size.

Conclusion

The sugar palm starch was successfully extracted from sugar palm tree. The important properties of sugar palm starch studied were the chemical properties, thermal properties, particle size and morphological surface. The starches isolated from sugar palm tree contained comparable amounts of amylose (37.60 %) which were higher than tapioca, sago, potato, wheat and maize. The results showed significant differences in the chemical content as well as in the granule sizes of sugar palm starch. Thermal characteristic studies using thermogravimetry analysis and differential scanning calorimetry showed that sugar palm starch was thermally stable than other starches.

Study on morphological surface indicated that sugar palm starch were rounded and oval-shaped. From this study we concluded that sugar palm starch derived from sugar palm tree have a potential to be used as a new alternative biopolymer.

ACKNOWLEDGEMENTS

The authors are grateful for the financial supports from Ministry of Higher Education under the 10th Malaysia Plan via the MyBrain15 program and to Universiti Putra Malaysia for their support during the research that have been conducted.

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