Characterization of starch nanoparticles

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Abstract. Nanomaterials already attract great interest because of their potential
applications in technology, food science and medicine. Biomaterials are
biodegradable and quite abundant in nature, so they are favoured over synthetic
polymer based materials. Starch as a nontoxic, cheap and renewable raw material is
particularly suitable for preparation of nanoparticles. In the paper, the structure and
some physicochemical properties of potato and cassava starch particles of the size
between 50 to 100 nm, obtained by mechanical treatment of native starch, were
presented. We demonstrated, with the aim of the Scanning Electron Microscopy
(SEM) and the non-contact Atomic Force Microscopy (nc-AFM), that the shape and
dimensions of the obtained nanoparticles both potato and cassava starch fit the
blocklets – previously proposed as basic structural features of native starch granules.
This observation was supported by aqueous solubility and swelling power of the
particles as well as their iodine binding capacity similar to those for amylopectin-type
short branched polysaccharide species. Obtained results indicated that glycosidic
bonds of the branch linkage points in the granule amorphous lamellae might be broken
during the applied mechanical treatment. Thus the released amylopectin clusters could
escape out of the granules. The starch nanoparticles, for their properties qualitatively
different from those of native starch granules, could be utilized in new applications.

1. Introduction
Numerous properties of materials depend on the size and internal structure of their constituents. Nanomaterials, due to the particle size in the range of nanometers, exhibit properties that are unique and qualitatively different from those of large-size particles. Biomaterials possess internal nanostructure, they are biocompatible and biodegradable therefore they are favoured over synthetic polymer based materials. Starch as a widely available raw material seems to be a very good substrate for preparation of nanoparticles. This carbohydrate polymer, composed of the glucose units, consists
of two molecular components: linear amylose and branched amylopectin. They are organized in alternating crystalline and amorphous lamellae in the granules [1,2]. Amylopectin side chain clusters are thought to make up the crystalline regions while amorphous lamellae are thought to contain amylopectin branch linkage as well as amylose chains, granular water and some other compound molecules. Crystalline and amorphous lamellae are grouped into larger elongated structures – blocklets of dimensions in the range of 20 – 500 nm [3]. Starch with heterogeneous granule size varied from less than 100 nm (nanoparticles) to a few µm (microparticles) could find many applications, such as: thickener or rheology modifier (in foods, paints, inks), adhesive or adhesive additives, a matrix material or filler in coating applications and biodegradable polymers, a carrier and slow-release agent in pharmacy, cosmetics and foods, for delivery of pesticides, fertilizers and chemicals in agriculture, in paper-making and packaging industry, etc. [4]. The average particle size of natural polysaccharides (from ~1 µm to > 100 µm) is determined by their origin and in most cases it cannot be influenced. Therefore, processing of native substrates is the only way to obtain starch with desired particle size distribution. In the paper, the structure and some physicochemical properties of potato and cassava starch particles of the size between 50 to 100 nm, obtained by mechanical depolimerization of native starch, were presented.

2. Experimental

2.1. Materials

Granular potato starch isolated in Nowamyl (Łobez, Poland) according to [5] and cassava starch, kindly supported by dr. Kuakoon Piyachomkwan from the Cassava and Starch Technology Research Unit at Kasetsart University Jatujak in Bangkok, was for 3 hours oven dried at 120°C. After such preparation, starch-ethanol suspensions were ground in a vibration mill following the already described procedure [6]. Mixture of the processed granules was separated by sedimentation into polysaccharide fractions and the fractions after 36 hours of sedimentation (about 15% of the mixture) were collected for further investigations.

2.2. Microscopic investigations

SEM images of the granule mixture before and after treatment, protected by thin layer of graphite, were taken with the scanning electron microscope SEM Jeol (JSM-5500LV). High-resolution non-contact atomic force microscopy (nc-AFM) was performed using a Park Scientific Instrument Autoprobe CP II model (California, USA) and the AFM Ultralevers tips of Veeco (Fig.1). Potato starch granules were spread on an adhesive tape fixed onto an AFM sample holder and examined under ambient conditions. For each starch sample images of several starch granules were collected. The particle size was assessed with the aim of Veeco IP II program.

Fig.1. The AFM microscope used for imaging of starch samples at ambient conditions
2.3. Physicochemical properties
Aqueous solubility, water holding capacity and iodine binding capacity of the particles and their BET surface area was determined by the methods described elsewhere [7].

3. Results and discussion
Mechanical processing of starch caused a severe damage to the granules what is presented in Fig.2 and 3 for potato and cassava starch, respectively. Initial granule population of about 50-80 µm of diameter consisted of the structural elements of the average size in the range of 200 -300 nm (Fig.4 for potato starch). It was found after the processing that about 15% of the granules of both kinds of starch form small irregular oblong species resembling the shape of structural elements previously observed in the native starch granules. Their shape and dimensions assessed by using the high resolution nc-AFM microscopy, are presented in the Figs.5,6 and 7.

Fig.2. SEM images of potato starch granules before (left) and after (right) the applied mechanical processing.

Fig.3. SEM images of cassava starch granules before (left) and after (right) the applied mechanical treatment.
According to the shape and the size in the range of 50 – 100 nm the particles might correspond to the polysaccharide blocklets released from the starch granules during the applied treatment.

Fig.4. High resolution nc-AFM images of native potato starch granule surface

Fig.5. High resolution nc-AFM images and dimensions of potato starch nanoparticles

Fig.6. SEM image of cassava starch nanoparticles
Fig. 7. High resolution nc-AFM images and dimensions of cassava starch nanoparticles

Such a conclusion was supported by the physicochemical properties determined for the starch nanoparticles (Table 1). In particular, an increasing of their aqueous solubility and swelling power with simultaneous decreasing of the iodine binding capacity compared to native starch indicated that the obtained nanostarch particles fit the amylopectine-type short branched species [8]. Some differences observed for potato in comparison with cassava particles could be attributed to botanical origin of the starch.

4. Summary
Mechanical treatment applied to potato and cassava starch resulted in formation of the particle mixture contained about 15% of nanoparticles with the size between 50 – 100 nm. The particles were characterized as amylopectin-type short branched species bundled into larger blocklets released from the granules crumbled in the process. The starch nanoparticles due to their susceptibility to chemical
reagents as well as properties qualitatively different from those of native starch granules, could be utilized in new applications, e.g. as suitable carriers in the drug and/or chemical delivery systems.

Table 1. Physicochemical properties determined for starch nanoparticles

| Potato starch          | Cassava starch        |
|------------------------|-----------------------|
| native nanoparticles   | native nanoparticles  |
| Blue Value (E635nm)    | 0.33 ±0.03            |
| Iodine binding capacity: E640/E525 | 1.32 |
| Branching characteristic: | Amylopectin-type short branched-glucans |
| Aqueous solubility at room temperature [%] | 0.48±0.05 | 37.50±0.05 |
| Swelling power [g H2O/g starch] | 1.70±0.10 | 12.75±0.10 |
| BET surface area [m2/g] | < 0.10 | 3.06±0.10 |

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