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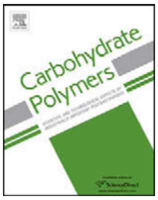

Short communication

Size controlled synthesis of starch nanoparticles by a simple nanoprecipitation method

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ABSTRACT

Starch nanoparticles of particle size range between 300 nm and 400 nm were synthesized by a simple nanoprecipitation method from native sago starch (*Metroxylon sagu*). Starch nanoparticles were formed by controlled precipitation through drop-wise addition of dissolved native starch solution to excess absolute ethanol. The size and shape of starch nanoparticles were modulated varying the synthesis parameters including the use of appropriate surfactant. Starch nanoparticles with mean diameter of about 150 nm were obtained in the presence of surfactants during precipitation. Both solvent and non-solvent systems used in the synthesis method were aqueous-based and the method was facile, and easy to perform as compared to other synthesis approaches previously reported.

1. Introduction

Starch is one of the natural occurring polymers which is biocompatible, biodegradable and shows bio-adhesion property. It is a polysaccharide that contains amylose and amylopectin (Pang, Chin, Tay, & Tchong, 2011). Due to its biodegradability, abundance and low cost, starch has been widely used in various applications such as water-soluble pouches for insecticides (Frederiksen, Hansen, Borggaard, & Pedersen, 2002), tissue engineering scaffolds (Gomes, Godinho, Tchalamov, Chunha, & Reis, 2002), excipients for tabletting and drug delivery carriers (Mahkam, 2010). Nano-sized starch particles have attracted much attention due to their unique properties that are different significantly from their bulk materials. Various synthesis methods have been attempted to prepare starch or starch derivatives nanoparticles. Starch nanoparticles with particles sizes of around 20–50 nm were synthesized by complex formation of starch–butanol followed by enzymatic hydrolysis of these starch–butanol complexes (Kim & Lim, 2009). However, due to the significant loss (85–90%) of the initial starch complex during hydrolysis process, the overall yield of the resulting starch nanoparticles was very low. Liu et al. reported the use of a high pressure homogenization method to prepare corn starch nanoparticles with yield of almost 100%. However, their synthesis method did not allow proper control of particle sizes (Liu, Wu, Chen, & Chang, 2009).

Due to its simplicity and reproducibility, the nanoprecipitation technique has been explored for the preparation of synthetic polymer nanoparticles such as poly(lactic acid) (PLA) and poly(lactic-co-glycolic acid) (PLGA) nanoparticles (Bilati, Allemann, & Doelker, 2005). In this paper, we have reported on the synthesis of starch nanoparticles with controllable particle sizes from native sago starch using the nanoprecipitation method. Starch nanoparticles were formed instantaneously in this one-step precipitation process. Starch nanoparticles of controllable particle size and shape were obtained by optimizing the precipitation conditions such as the rate of precipitation and the use of surfactants during precipitation.

2. Materials and methods

All chemicals were of reagent grade and were used without further purification. Ultrapure water (~18.2 MΩ, 25 °C) was obtained from a Water Purifying System (ELGA, Model Ultra Genetic). Sodium hydroxide and Tween 80 were purchased from Merck. Cetyl trimethylammonium bromide was obtained from J.T. Baker. Native sago starch powder was obtained from a local grocery store.

2.1. Preparation of sago starch nanoparticles

Starch nanoparticles were obtained by addition of starch solution into excess absolute ethanol under controlled conditions. In this study, the NaOH/urea (NU) (0.8:1 wt%) solution mixture was used as a solvent system for the dissolution of native sago starch. Generally 1 wt% of native sago starch solution was prepared by dissolving native sago starch powder in the NU solvent at ambient conditions. An aliquot of sago starch solution (1 mL) was added drop-wise into a fixed quantity of absolute ethanol (10 mL, 15 mL and 20 mL) which was continually stirred using a magnetic stirrer at

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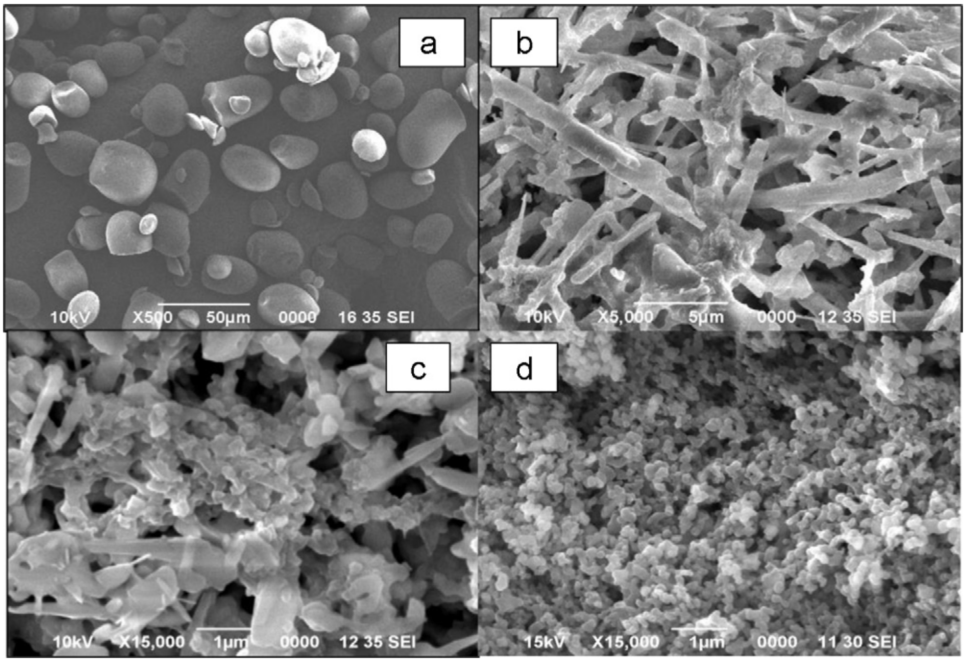

Fig. 1. SEM micrographs of (a) native starch granules; and starch nanoparticles prepared by addition of 1 mL of 1% starch into (b) 5 mL (c) 10 mL and (d) 20 mL of absolute ethanol.

a constant stirring rate. The resulting mixture was then centrifuged and the supernatant was removed to obtain the regenerated starch nanoparticles, which were rinsed 3 times with absolute ethanol to remove NaOH and urea.

Stable suspension of starch nanoparticles were formed by dropwise addition of dissolved starch/surfactant solution mixture into absolute ethanol under continuous stirring at a constant rate. The suspension was continuing stirred for another 30 min at room temperature before it was filtered and washed multiple times with absolute ethanol to remove any free surfactants.

2.2. *Characterization of sago starch nanoparticles*

The morphology of sago starch nanoparticles was investigated using a scanning electron microscope (SEM) (JEOL Model JSM 6390LA). The average particle size of the starch nanoparticles was determined by randomly measuring a minimum of 50 particles using the “SmileView” software.

3. Results and discussion

The NaOH/urea (NU) solvent system was chosen as it had been reported to dissolve chitin and cellulose directly and effectively (Jin, Zha, & Gu, 2007). Furthermore, this solvent system is non-toxic, environmental friendly and inexpensive. The presence of NaOH breaks the intermolecular and intramolecular hydrogen bonding of starch molecules, whereas urea plays an important role in preventing self-association of starch molecules, leading to enhanced solubility of native sago starch powder.

3.1. *Effect of precipitating medium*

Fig. 1a shows the SEM micrograph of native sago starch granules used in this study. The size of the sago starch granules ranged from 2 to 50 μm. The granular structure of sago starch was completely disrupted upon dissolution in the NU solvent system to form homogeneous starch solution. Starch nanoparticles were subsequently precipitated by controlled addition into absolute ethanol. The ratios of starch solution to ethanol used in the precipitation were observed to have a significant impact on the morphology of starch nanoparticles formed. The precipitated starch particles were observed to be fibrous in shape when the volume ratio of starch solution to ethanol 1:10 (v/v) was used (Fig. 1b). A mixture of spherical starch nanoparticles and elongated fiber-like particles were formed when the volume ratio of starch solution to ethanol was changed to 1:15 (Fig. 1c). However, when the volume ratio of starch solution to ethanol was further changed to 1:20, the sample was observed to consist of mainly spherical shaped starch nanoparticles with particle sizes ranged between 300 nm and 400 nm.

3.2. *Effect of surfactant*

The effect of adding surfactants, hexadecyl (cetyl) trimethylammonium bromide (CTAB) and Tween 80 on the mean particle sizes of starch nanoparticles formed was investigated. The morphologies of precipitated starch nanoparticles precipitated from dissolved starch solution in the presence of surfactant (4% CTAB or 4% Tween 80) are shown in Fig. 2. It was observed that the mean sizes of starch nanoparticles were reduced to around 250–300 nm and 150–200 nm in the presence of CTAB and Tween 80, respectively. The presence of surfactants during the precipitation process could have limited the growth of starch nanoparticles and thus the observed particles of reduced mean sizes. A smaller mean size range of starch nanoparticles was obtained in the presence of Tween 80 surfactant as compared to that of CTAB surfactant. Since starch is a non-ionic polysaccharide, interactions between starch and CTAB or Tween-80 would be dominated by hydrophilic interactions (Lundqvist, Eliaason, & Olofsson, 2002a, 2002b). Tween-80 is comparatively more hydrophilic than CTAB, and would interact stronger with starch molecules, and hence starch nanoparticles of smaller sizes were precipitated.

As shown in Fig. 3, more discrete starch nanoparticles were obtained when CTAB was present in the starch solution as compared to that of CTAB present in ethanol solution. When CTAB was added to starch solution before precipitation, starch molecules

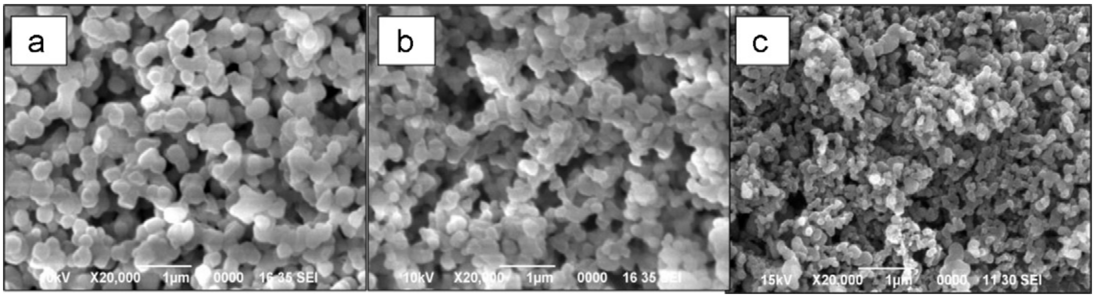

Fig. 2. SEM micrographs of precipitated starch nanoparticles prepared by addition of 1 mL of 1% starch into 20 mL of ethanol (a) without surfactant, (b) with 4% of CTAB, and (c) with 4% of Tween 80.

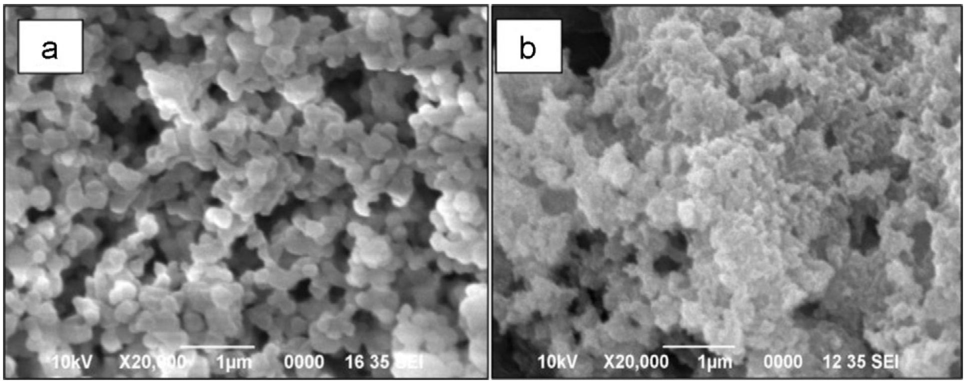

Fig. 3. SEM images of precipitated starch prepared by addition of (a) 1 mL of 1% starch with 4% CTAB into 20 mL of absolute ethanol; (b) 1 mL of 1% starch solution into 20 mL of absolute ethanol with 4% of CTAB.

which are hydrophilic in nature were interact with the CTAB molecules. CTAB would thus act as a surfactant which reduced the gelation rate of starch nanoparticles, and the gelation of starch particles was observed to occur only after several weeks. However, when CTAB was present in ethanol solution, the starch molecules had precipitated quickly in ethanol before mixing thoroughly with CTAB molecules, the precipitated starch nanoparticles would gel rapidly (within a few hours) upon absorption of moisture from the air (Fig. 3b).

4. Conclusions

In this study, starch nanoparticles were being synthesized by precipitating dissolved starch solution in absolute ethanol under controlled conditions. The synthesis method used is simple, fast and easy to perform. The mean sizes of starch nanoparticles could be modulated by the synthesis parameters such as the use of surfactants during the synthesis process.

Acknowledgement

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