



# Preparation of starch nanospheres through hydrophobic modification followed by initial water dialysis



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## ABSTRACT

Starch nanospheres smaller than 200 nm were produced from hydrophobically modified starch by using initial water dialysis method. The hydrophobic modification of starch was performed by using octenyl succinic anhydride (OSA). The resultant starch nanospheres were characterized by using Fourier transformation infrared (FTIR) spectroscopy, <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy and fluorescence spectroscopy, scanning electron microscopy (SEM) and dynamic light scattering (DLS). Effects of degree of substitution (DS) in OSA-starch, initial water content and OSA-starch concentration on morphology and particle size of starch nanospheres were evaluated. The SEM micrographs showed that starch nanospheres with spherical shape and sharp edge can be produced at DS values  $\geq 0.67$ . The particle size of starch nanospheres decreased significantly ( $P < 0.05$ ) with increase in DS of OSA-starch and increase in the initial water content, whereas the particle size increased significantly ( $P < 0.05$ ) with the increase in the concentration of OSA-starch. These OSA-starch nanospheres can be preferentially used to microencapsulate hydrophobic drugs.

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## 1. Introduction

Nanoparticles (10–1000 nm) can be obtained in various morphologies such as nanospheres, nanocapsules and nanoliposomes (Jung et al., 2000; Pinto Reis, Neufeld, Ribeiro, & Veiga, 2006). There has been growing interest in preparing biodegradable and non-toxic nanoparticles as vehicles for drug delivery for biomedical applications (Lemarchand, Gref, & Couvreur, 2004). Partial hydrophobic modification of pullulan (Jung, Jeong, Kim, & Kim, 2004), chitosan (Vieira, Moscardini, Tiera, & Tiera, 2003; Yang et al., 2008), and dextran (Aumelas, Serrero, Durand, Dellacherie,

& Leonard, 2007; Liebert, Hornig, Hesse, & Heinze, 2005) has been used to produce self-assembled nanospheres.

Starch is suitable material to produce nanoparticles for industrial applications because it is non-toxic, biodegradable, biocompatible and readily available in reasonable price (Rodrigues & Emeje, 2012). Starch nanoparticles are commonly produced using nanoprecipitation (Tan et al., 2009; Tay, Pang, & Chin, 2012), acid hydrolysis (Angellier, Choïnard, Molina-Boisseau, Ozil, & Dufresne, 2004) and emulsification (Jain, Khar, Ahmed, & Diwan, 2008; Shi, Li, Wang, Li, & Adhikari, 2011). However, these methods have disadvantages such as they take long time to produce nanoparticles, leave behind large quantity of organic solvent, require large amount of emulsifiers and particle size distribution is usually quite broad.

Dialysis is an effective way of producing nanospheres (Liu et al., 2007; Namazi, Fathi, & Dadkhah, 2011). This method is based on the exchange of solvent and water through diffusion during the

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dialysis process. The polymer precipitates into nanoparticles due to the solvent–water exchange. This method has many advantages, for example, the size distribution of nanoparticles can be controlled within a narrow range and the solvent can be completely removed at ambient condition.

The amphiphilic characteristic of a biopolymer is responsible for producing self-assembled nanospheres through the dialysis process. In aqueous solution, the amphiphilic polymers self-assemble spontaneously into a core–shell nanospherical (micellar) structure. This self-assembly is driven by intra- or intermolecular associations between hydrophobic moieties, primarily to minimize the free energy at the interface (Letchford & Burt, 2007). The formation of polymeric nanoparticles in water results from self-assembly of nanospheres containing hydrophobic domains in the core and hydrophilic domains in the shell. The micellar core creates a microenvironment which can contain many hydrophobic drugs. At the same time, the hydrophilic micellar shell provides a stabilizing interface between the hydrophobic core and the aqueous medium (Song, Zhang, Gan, Zhou, & Zhang, 2011).

Octenyl succinic anhydride (OSA)-starch is prepared by esterification of native starch or starch derivatives using OSA. It is one of the most important amphiphilic starch derivatives (Liu et al., 2008). Through esterification, the hydrophobicity of OSA is introduced and the hydrophilicity of starch backbone is retained. Although many studies on the esterification of starch have been reported, the degree of substitution (DS) of OSA-starch for food applications is typically low, and the highest DS value of OSA-starch is reported to be of the order of 0.1 in the literature (Shogren, Viswanathan, Felker, & Gross, 2000; Viswanathan, 1999). This could be explained by two reasons. Firstly, starch is polymeric molecule and forms granular structure. This means that the granule structure restricts the diffusion of reactants to the interior of the granule due to which the reaction occurs mostly on the surface. Secondly, the reaction is performed under heterogeneous conditions, which reduces the reaction efficiency between OSA and starch. For preparing OSA-starch with high DS, Shogren et al. (Shogren, 2003) performed the modification with OSA under high temperature/pressure conditions and DS of about 0.5 was achieved at 180 °C. Another way to obtain OSA-starch with a DS of 0.3 was performed using a microwave-assisted modification (Biswas, Shogren, Kim, & Willett, 2006). However, these methods are confined to improve the DS. Recently, Wang, Li, et al. (2011) used pyridine as reaction medium. These authors obtained DS values of 0.2–1.3 using OSA/starch weight ratios up to 5/1. This is because pyridine increases the initial reactivity of the starch grains and also acts as a catalyst in starch and OSA reaction as it forms a succinyl-pyridinium intermediate. This intermediate much more readily reacts with hydroxyl groups than the non-activated OSA molecules (Viswanathan, 1999).

Despite the above mentioned advantages of preparing self-assembled nanospheres using dialysis method, there are no studies on the formation and characteristics of self-assembled OSA-starch nanospheres prepared using dialysis method. This is mainly due to low degree of substitution (DS) of OSA in starch as mentioned above. The low DS tends to favor supramolecular interactions through hydrogen bonds. These interactions lead to aggregation and ultimate collapse of the nanoparticles (Hornig, Heinze, Hesse, & Liebert, 2005).

In this study, we prepared OSA-starch with high DS through esterification of waxy corn starch with OSA using pyridine as the solvent. Subsequently, we prepared self-assembled nanospheres from the amphiphilic OSA-starch which had high DS. The initial water dialysis method was used to produce these nanospheres. The starch nanospheres produced in this way had narrow size distribution. We also quantified and explained the effect of DS, initial water content, concentration of OSA-starch on the particle size distribution and microstructure of the OSA-starch nanospheres.

## 2. Materials and methods

### 2.1. Materials

Waxy corn starch was purchased from Dezhou Dacheng Food Co., Ltd. (Shandong, China). Octenyl succinic anhydride (OSA) was obtained from Nanjing Golden Chemical Co., Ltd. (Nanjing, China). Dimethyl sulfoxide (DMSO) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China) and was dried over molecular sieves and then vacuum-distilled. Pyridine was purchased from Chinasun Specialty Products Co., Ltd. (Jiangsu, China). Dialysis tube with a molecular weight cut-off of 8000–15,000 g/mol was purchased from MYM Biological Technology Company (USA). DMSO- $d_6$  (99.9% atom D) and trifluoroacetic acid- $d_1$  (TFA- $d_1$ , 99.5% atom D) were from Cambridge Isotope Laboratories, Inc. (USA). All other chemicals were of analytical grade and were used as received.

### 2.2. Preparation of OSA-starch

OSA-starch was used as the main material to synthesize nanoparticles. It was prepared by modifying partially hydrolyzed waxy maize starch with *n*-octenyl succinic anhydride.

Partially hydrolyzed waxy maize starch was prepared by an acid-alcohol treatment (Chang, Lin, & Lii, 2004). One hundred grams of waxy maize starch (dry basis) were suspended in 400 mL ethanol solution (90%, v/v). The reaction was started by adding 4 mL concentrated HCl (36%, w/w) and heating the mixture to 65 °C and maintaining this temperature for 1 h. The reaction was stopped by adding 28 mL of 1 mol/L  $Na_2CO_3$  solution. The fully reacted mixture was cooled in an ice-bath for 5 min and centrifuged at 3500 rpm for 5 min. The precipitate was washed four times with ethanol (50%, v/v) and precipitated through centrifugation. The final precipitate was dried at 40 °C using a fan forced oven for 24 h.

The partially hydrolyzed starch (15 g, d.b.) was suspended in 150 mL pyridine solution in a 250 mL three-neck round bottom flask. This suspension was stirred using a mechanical stirrer at 85 °C for 2 h to activate the starch. Subsequently, 15 g (OSA-to-starch ratio = 1:1) to 75 g (OSA-to-starch ratio = 5:1) liquid OSA was added into the flask through a funnel. The reaction between OSA and starch was allowed to continue for 2.5 h at 85 °C. Once the reaction was completed, the flask together with its content was cooled to room temperature. The OSA-starch obtained in this way was washed three times with distilled water and twice with 70% (v/v) alcohol by means of centrifugation. This fully washed OSA-starch precipitate was oven dried at 40 °C for 24 h.

### 2.3. Synthesis of starch nanospheres

As mentioned in Section 1, dialysis is one of the most extensively used methods of producing self-assembled polymer nanospheres. In this work, starch nanospheres were synthesized by using water dialysis method as reported by Liu et al. (2007) with some minor modifications.

For a typical batch, a sample of 20 mg OSA-starch was placed in 10 mL of DMSO and heated to 95 °C in a water bath until the solution became clear. Then, 10 mL distilled water (referred to as initial water) was added into the OSA-starch–DMSO solution under continuous stirring. Subsequently, this mixture was transferred to the dialysis tube (molecular cut off 8000–15,000 g/mol) and dialyzed against 1.0 L of distilled water at intervals of 2 h in the first 6 h, then at intervals of 6 h during the following 42 h. This suspension containing OSA-starch nanospheres was stored at 4 °C before further analysis.

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