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Green preparation and characterisation of waxy maize starch nanoparticles through enzymolysis and recrystallisation

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A B S T R A C T

Waxy maize starch was treated by a facile and green enzymolysis procedure to fabricate starch nanoparticles (StNPs). The yield of StNPs was raised to 85% by pullulanase treatment, and the preparation duration was two days. Morphology (SEM, TEM), crystalline structure (XRD), thermal gravimetry analysis (TGA), and the group changing (FTIR) of StNPs prepared with different starch concentrations (10%, 15%, 20% and 25%, w/v) were investigated. Compared with native starch, the topography of all StNPs exhibited irregularly-shaped fragments, the particle diameters decreased from several μm to about 60–120 nm, and the crystal pattern changed from A-type to B + V-type. The StNPs prepared with 15% starch slurry had the highest degree of crystallinity at 55.41%. The eco-friendly prepared nanoparticles could be widely used in biomedical applications and development of new materials.

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1. Introduction

Among the carbohydrate polymers, starch is an abundant, inexpensive, naturally renewable, and biodegradable polysaccharide. Starch is composed of two different components, linear amylose and branched amylopectin. For waxy maize starch, there is 95–99% amylopectin and 1–5% amylose. Since starch is a low-cost versatile biopolymer, it has been widely used in food and in many industrial applications (Jobling, 2004).

In recent years, the preparation and application of biodegradable nanocrystals and nanoparticles have been attracting more research interest. As a typical green biodegradable natural polymer, starch is a good candidate for producing nanocrystals and nanoparticles. Recently, LeCorre, Bras, and Dufresne (2010) published a comprehensive review on starch nanoparticle preparation, characterisation, and applications. Starch nanoparticles or nanocrystals have many potential applications in various fields, such as plastic fillers (Angellier, Molina-Boisseau, & Dufresne, 2005), food additives, drug carriers, implant materials (Thielemans, Belgacem, & Dufresne, 2006), biodegradable composites, and so on. Starch nanoparticles also have a great potential for use in papermaking, surface sizing, coating and paperboard as a biodegradable adhesive in place of petroleum-based adhesives. In addition, starch nanoparticles have many advantages over traditional cooked starch, due to properties such as low viscosity of suspension, even at very high solid concentration (up to 30%, w/v), and higher bonding strength (Bloembergen, Kappen, & Beelen, 2005).

Starch nanocrystals and nanoparticles can be prepared in three different ways: acid or enzymatic hydrolysis, regeneration, and mechanical treatment (LeCorre et al., 2010). Acid hydrolysis is the typical way to generate starch nanocrystals (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004). Their preparation by acid hydrolysis was optimised previously (García, Ribba, Dufresne, Aranguren, & Goyanes, 2011). Recent publications suggest that ceramic membrane filtration for isolating starch nanocrystals can improve the yield (LeCorre, Bras, & Dufresne, 2011). Enzyme treatment before acid hydrolysis can reduce the duration of the treatment (LeCorre, Vahanian, & Dufresne, 2012). Platelet-like starch nanocrystals with a length of 20–40 nm and a thickness of 4–7 nm (Dufresne, 2008) were produced using the above methods. However, the acid hydrolysis method is difficult for industrial applications due to its negative environmental impact. Nanosized starch particles can be also generated by precipitating starch solution with some organic solvents. Ma, Jian, Chang, and Yu (2008) used ethanol as a precipitant to precipitate pre-cooked native starch and obtained StNPs in the range of 50–100 nm. By using a combination of complex formation with n-butanol and enzymatic hydrolysis, Kim and Lim (2009) prepared StNPs with a size of 10–20 nm, while Bastioli, Floridi, and Tredici (2009) filed a patent for producing StNPs by combining modified starch with complexing agents followed by mixing with a hydrophobic polymer. StNPs

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can also be prepared by processing starch granules with mechanical and thermal treatment. Liu, Wu, Chen, and Chang (2009) proposed a simple and environmentally-friendly technique using a high-pressure homogenisation method for preparing StNPs. Experimentally, 5% starch slurry was passed several times through a specially designed microfluidizer under high shear pressure. They found that the starch particle size could be reduced from 3–6 μm to 10–20 nm after 20 passes. By combining a high-pressure homogenisation technique with miniemulsion cross-linking, Shi, Li, Wang, Li, and Adhikari (2011) prepared sodium trimetaphosphate (STMP) cross-linked StNPs. As a purely mechanical treatment process within a water system, the higher pressure homogenisation method is environmentally friendly. However, as only low concentration starch slurry could be processed for homogenisation, the yield is still not high.

In order to adopt green chemistry techniques to prepare StNPs, we wish to avoid using chemical reagents. Pullulanase, also known as amylopectin 6-glucanohydrolase, could cleave alpha-glucan polysaccharides and is widely used in the starch industry. After treatment with pullulanase, waxy maize starch amylopectin is transformed into short linear glucans that can achieve reassociation and retrogradation. Waxy maize starch was debranched by pullulanase, retrogradated at room temperature, and dried at 45 °C overnight to produce resistant starch (RS), but the particle size was approximate 0.8–2 μm (Shi, Chen, Yu, & Gao, 2013). Interestingly, we found the retrogradation of the branched short linear glucans could easily form StNPs at low temperature through freeze-drying. However, to the best of our knowledge, there are as yet no publications reporting the preparation of StNPs through enzymolysis and recrystallisation.

Fabrication of StNPs using enzyme hydrolysis is a promising method owing to its complete biodegradability, low cost, ready availability, and renewability. Here we wish to report the preparation of StNPs using pullulanase which could avoid the use of a chemical reagent and simultaneously increase the yield. Some physical properties of StNPs that were produced will also be presented.

2. Experimental

2.1. Materials

Waxy maize starch was provided by National Starch Co., Ltd. (Guangdong, China) (98% amylopectin). Disodium hydrogen phosphate (Na_2HPO_4) and Citric acid ($C_6H_8O_7$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pullulanase (E.C.3.2.1.41, 6000 ASPU/g, 1.15 g/mL, where ASPU is defined as the amount of enzyme that liberates 1.0 mg glucose from starch in 1 min at pH 4.4 and 60 °C) was supplied by Novozymes (China) Investment Co. Ltd. (Bagsvaerd, Denmark).

2.2. Preparation of StNPs with pullulanase

A given weight of waxy maize starch was dispersed in 200 mL of buffer solution (pH 5.0) with different starch concentrations of 10%, 15%, 20%, 25% (w/v) referred to as SC10, SC15, SC20, and SC25, respectively. In order to fully gelatinize the starch, the starch slurry was cooked in boiling water with vigorous stirring for 30 min. The temperature of cooked waxy maize starch was adjusted to 58 °C and pullulanase (30 ASPU/g of dry starch) was added. After an 8 h incubation period at 58 °C, the reaction was stopped by heating at 100 °C for 30 min to inactivate the pullulanase, followed by cooling to room temperature. Then, the solutions were stored at 4 °C for 8 h. The suspensions were washed several times with distilled water until neutrality and then dried by two different methods. In the first method air drying at 60 °C for 48 h was used to obtain starch microparticles (StMPs). In the second, freeze drying was used to obtain StNPs. The yield of StNPs was calculated by dividing the weight of freeze-dried by precipitate initial dry weight of waxy maize starch.

2.3. Scanning electron microscopy (SEM)

Native and StNP samples were mounted on carbon sample holders using double-side sticky tape (native starch) and carbon coat (StNPs). They were observed using a JEOL JMS 7600F scanning electron microscope (Akishima, Japan) with the SEM mode at 2 kV accelerating voltage. Micrographs at 3000× (native starch) and 30 000× (StNPs) magnification were presented.

2.4. Transmission electron microscopy (TEM)

Transmission electron micrographs of StNPs were taken with a Hitachi (Tokyo, Japan) 7650 transmission electron microscope with an acceleration voltage of 80 kV. StNPs were deposited on a carbon-coated grid without any treatments.

2.5. X-ray diffraction (XRD)

Native starch and StNPs samples were stored for 24 h in a sealed container at a relative humidity of 85% to achieve constant moisture content. XRD patterns were measured at room temperature. A Siemens D-5000 diffractometer (Karlsruhe, Germany) using Cu Kα radiation (λ = 1.543) and a secondary beam graphite monochromator was operated at 40 kV and 30 mA. Intensities were measured in the 4–45° 2θ range with a 0.03° step size and measuring time of 2.0 s per point. The relative crystallinity of the samples was quantitatively estimated following the method adapted from Nara and Komiya (1983), also called the "two-phase" method. A curve connecting the peaks' baseline was plotted on the diffractogram. The area above the curve was assumed to correspond to the crystalline domains, and the lower area was assumed to correspond to the amorphous part.

2.6. Thermogravimetric analyses (TGA)

TGA were conducted via a synchronous thermal analysis (Netzsch STA449C/4/G, Selb, Germany). Samples for thermal characterisation (native starch, SC10, SC15, SC20, SC25) were previously stored at 33% relative humidity ($MgCl_2$ saturated solution) for five days. Samples weighing 3–6 mg were heated from 25 °C to 450 °C at a heating rate of 10 °C min^{-1} in a dynamic atmosphere of synthetic air (80% N_2 and 20% O_2) with flow rate of 100 mL/min. The sample weight was plotted as a function of temperature for all samples. Two replicates were analysed for each sample.

2.7. Fourier transform infrared spectroscopy analysis (FTIR)

FTIR spectra were recorded using a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA). StNPs samples were collected using the KBr pellet method. The resolution was 4 cm^{-1} and there were a total of 32 scans.

2.8. Statistical analysis

Each measurement was carried out using at least three fresh, independently prepared samples. The results were reported as the mean value and standard deviation. The data were subjected to analysis of variance (ANOVA) using the SPSS V.12 statistical software package (SPSS Inc., Chicago, IL). Duncan's multiple range test was also applied to determine the difference of means from ANOVA, using a significance test level at 5% (p < 0.05).

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