



Short communication

Preparation of donut-shaped starch microparticles by aqueous-alcoholic treatment



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ABSTRACT

A simple method for producing donut-shaped starch microparticles by adding ethanol to a heated aqueous slurry of corn starch is presented. The obtained microparticles were analysed by SEM, XRD and DSC. The average size of microparticles was $14.1 \pm 0.3 \mu\text{m}$ with holes of an average size of $4.6 \pm 0.2 \mu\text{m}$. The crystalline arrangement of the microparticles was of a V-type single helix. The change in crystallinity from A-type of the starch granules to a more open structure, where water molecules could penetrate easier within the microparticles, substantially increased their solubility and swelling power. The microparticles exhibited a higher gelatinization temperature and a lower gelatinization enthalpy than did the starch granules. The donut-shaped microparticles were stable for more than 18 months and can be used as a carrier of an active compound or as a filler in bioplastics.

1. Introduction

Starch is a natural polymer of glucose that is widely available, biodegradable and biocompatible. Depending on the botanical source, the starch granules are typically of many micrometres in size and of different shapes. There are several strategies to increase the surface area of starch granules and thereby their processability and performance. For example, in the acid hydrolysis treatment the particle size of starch is reduced and its degree of crystallinity is increased, which leads to a decrease of the swelling power and pasting temperature and retards the development of viscosity (Gonçalves, Noreña, da Silveira, & Brandelli, 2014). Starch structures with a high area to volume ratio, i.e. micro/nanoparticles, have been used as a carrier to modulate the release of active compounds (El-Feky, El-Rafie, El-Sheikh, El-Naggar, & Hebeish, 2015). The size and the shape of the micro/nanoparticles, as well as their properties and release characteristics, depend on the preparation method (Xie, Pollet, Halley, & Avérous, 2013).

A granular cold water-soluble starch has been used as a solid biodegradable matrix to encapsulate substances, such as ethylene (Shi, Fu, Tan, Huang, & Zhang, 2017), atrazine (Chen & Jane, 1995), and fatty acids (Lay Ma, Floros, & Ziegler, 2011). These microparticles are generally obtained by an alcoholic-alkaline treatment, where the sodium hydroxide disrupts the intermolecular hydrogen bonds of starch macromolecules, while ethanol inhibits the swelling of the granules

(Chen & Jane, 1994). Although the overall integrity of the granules is preserved, the starch granules are completely deformed and the size is increased after the treatment.

In this communication, a simple and novel method for the preparation of donut-shaped microparticles is described, in which heated starch slurry is precipitated by addition of ethanol. The morphology, structure, thermal and swelling properties of the microparticles were studied. The produced microparticles are intended to be used mainly as a carrier of active compounds or filler for bioplastics; both uses could be combined for active food packaging applications.

2. Materials and methods

2.1. Materials and reagents

Corn starch, composed of 25% amylose, was supplied by Roquette Freres S. A. (France). Ethanol was purchased from Scharlau (Spain).

2.2. Preparation of starch microparticles

The microparticles preparation from corn starch granules was performed according to the method proposed by Ma, Jian, Chang, and Yu (2008) with modifications. In short, 8 g of starch were added to 150 ml of Milli-Q water. The mixture was heated at 66°C , below the

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gelatinization temperature, under constant stirring at 500 rpm for 1 h. Then, 150 ml of absolute ethanol were added to the starch slurry during 75 min (2 ml/min), using a diaphragm pump (SIMDOS 02, KNF Neuberger, Switzerland). The suspension of starch microparticles was cooled to room temperature, and a further 150 ml of ethanol were added dropwise under constant stirring at a flow rate of 3 ml/min. Finally, the microparticles were washed with ethanol to remove water and then dried in a forced air circulation oven at 50 °C.

2.3. Scanning electron microscopy

The morphology of the starch microparticles was characterized, using a Carl Zeiss ultra plus field emission scanning electron microscope (FESEM) operated at 3 kV (Carl Zeiss, Germany). The particles were previously sputter-coated with iridium, using a QUORUM Q150T-S turbo-pumped sputter coater (Quorum Technologies Ltd, UK).

2.4. X-ray diffraction

The XRD spectra were recorded, using a Bruker Endeavour diffractometer (model D4/max-B, Germany) with Cu K α radiation (40 kV and 20 mA). The measurements were taken over a 2 θ range of 5–35° at steps of 0.02° and 1 s time steps.

2.5. Differential scanning calorimetry (DSC)

The gelatinization properties of starch microparticles and the corn starch granules were determined in triplicate by a Pyris-1 DSC (Perkin Elmer, Norwalk, CT, USA). About 2.0 mg of the starch sample (dry basis) were weighed into an aluminium pan and 6.0 μ l of deionized water were added and then the pan was hermetically sealed. The DSC scans were performed from 40 to 120 °C under N₂ atmosphere (20 ml/min) at 5 °C/min. An empty pan was used as reference. For the gelatinization process onset (T_o), gelatinization (T_g), and offset (T_{end}) temperatures, as well as the enthalpy of gelatinization (ΔH_g), were determined.

2.6. Solubility and swelling properties

Solubility index (%) and swelling power (g/g) were measured in triplicate, using the method reported by Castaño et al. (2014). Briefly, suspensions of starch microparticles and granules were heated separately at 60 °C for 30 min, followed by centrifugation at 4400 rpm for 30 min. The supernatant was decanted and dried overnight at 70 °C. The dried soluble solid was weighed to determine the solubility index (Eq. (1)).

$$\text{Solubility index (\%)} = \frac{\text{Weight of the dried soluble starch}}{\text{Total weight of the starch}} \times 100 \quad (1)$$

The solid residue of centrifugation was weighed for the determination of the swelling power (Eq. (2)).

$$\text{Swelling power} = \frac{\text{Weight of solid residue}}{\text{Total weight of the starch}} \quad (2)$$

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

The thermal treatment of the starch slurry, followed by the addition of ethanol as precipitant, produced donut-shaped microparticles as can be observed in Fig. 1(A, B and C). The size of the particles, measured directly from the SEM micrographs, using the ImageJ software, was in the same range of the corn starch granules, (5–25 μ m, Fig. 1E). The size distribution of the microparticles in Fig. 1(D) showed a defined peak

centred at 14.1 μ m and a range between 4.6 and 24.1 μ m. The distribution of the size of the central hole of the donut-like structure showed a defined peak at 4.6 μ m and ranged from 2.3 to 8.2 μ m. The shape of the central hole depended on the microparticle size. The central hole of particles lower than 12 μ m was round (Fig. 1B) whereas, for larger particles, the hole appeared deformed and collapsed (Fig. 1C). Almost all the microparticles displayed a central hole, although in some cases the hole was not well formed and the particles only exhibited a deep-concave geometry (Fig. 1A). The central hole is formed by the removal of ethanol on drying and is associated with the hilum of starch granules (Jane, Craig, Seib, & Hosene, 1986). In the hilum, the starch macromolecules (amylose and amylopectin) are loosely packed and a cavity is also found which is connected to the surface pores by channels (Jane, 2009). The pores and channels give water molecules accessibility to the hilum, allowing the hydration and swelling of starch granules from the inside out. When ethanol is added, inclusion complexes are formed and the granules shrink by dehydration. The water transfers through the channels from the centre of the granule to the periphery, leading to the flattening of the swelling granule. On drying at 70 °C, ethanol is removed and the central cavities “dry out”, yielding the donut-shaped microparticles.

The donut-shaped microparticles presented a rough surface with a lamella structure, similar to normal corn starch granules after chemical surface gelatinization, with a degree of 84% (Pan & Jane, 2000). The morphology of the microparticles suggests that the supra-macromolecular packing of granules did not completely break down after the thermal treatment. An analogous morphology was described for granular cold water-soluble starch prepared by an alcoholic-alkaline method at ambient pressure (Majzoobi, Kaveh, Blanchard, & Farahnaky, 2015). However, the central cavity of these particles was not well defined and their surfaces were smooth. Another difference between the donut-shaped microparticles and granular cold water-soluble starch is their size. It is approximately 2–4 times larger than the size of the original starch (Shi et al., 2017).

It is also noteworthy that the obtained microparticles maintained their morphology after more than 18 month of storage and after redispersion in ethanol.

3.2. X-ray diffraction (XRD)

In order to investigate the structural changes of the donut-shaped microparticles with respect to corn starch granules, their X-ray patterns were analysed. The starch granules had A-type crystallinity, showing well defined diffraction peaks at around 15°, 17°, 18° and 23° (Fig. 2). These peaks almost disappeared for the microparticles. However, two broad peaks at 13° and 20° were observed which are characteristics of a V-type single helix crystalline arrangement (Shi et al., 2017). During the swelling of the granules, uncoiling or dissociation of the double helix structure of amylopectin occurred, and the order of the crystalline lamella was destroyed. Ethanol restricts the swelling of the granules and forms inclusion complexes with amylose and long branch chains of amylopectin, generating the V-type single helix structure. Jane et al. (1986) reported similar X-ray diffraction patterns for cold water-soluble corn starch and proposed that, during heating of the dispersion of corn starch in aqueous alcohol, the double helical structures of both amylose and amylopectin were converted into a single helix.

3.3. Differential scanning calorimetry (DSC)

The DSC curves of the starch granules and the donut-shaped microparticles displayed typical endothermic peaks corresponding to the gelatinization of starch (Fig. 3). The thermal parameters obtained for the starch granules (Table 1) were in the same range as other corn starch varieties (de La Rosa-Millán, Agama-Acevedo, Jimenez-Aparicio, & Bello-Pérez, 2010). The microparticles exhibited a higher onset and gelatinization temperature, and a lower gelatinization

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