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Production and Characterization of Starch Nanoparticles

Normane Mirele Chaves Da Silva,
Fernando Freitas de Lima,
Rosana Lopes Lima Fialho,
Elaine Christine de Magalhães Cabral Albuquerque,
José Ignacio Velasco and Farayde Matta Fakhouri

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Abstract

In recent years, the increasing interest in nanomaterials of natural origin has led to several studies in the area of nano-sized particles from natural polysaccharide polymers, such as cellulose, starch, and chitin. These nanomaterials are used especially as a reinforcement in a polymeric matrix to improve the mechanical and barrier properties of the materials. Starch is a sustainable, abundant biopolymer produced by many plants as a source of storage energy; the main uses of starch are as food and industrial applications. However, recently their use as filler in polymeric matrix (nanoparticles) has attracted attention. Starch nanoparticles (SNPs) can be produced by many methods, using chemical, enzymatic, and physical treatments. The size distribution, crystalline structure, and physical properties of the SNPs may vary from one method to another. These nanoparticles are a very interesting alternatives not only for the polymeric filler but also for the renewability and biodegradability, since they show characteristics inherently of starch granules.

Keywords: methods, nanostarch, nanotechnology

1. Introduction

Nanotechnology is considered a study which involves science, medical, engineering, and technology at the nanoscale level; basically, nanotechnology involves the use of nanoparticles

ranging from 1 to 100 nm size [1]. In recent years, the use of nanotechnology for applications in the food industry has become more apparent, such as protection against biological and chemical deterioration, increasing bioavailability, enhancement of physical properties, and others [2]. However, the high cost of nanotechnology can make it difficult to its application in commercial scale. Therefore, the search for alternative materials and cheap to be used in the nanotechnology has been studied. Starch being a biodegradable natural polymer is a great alternative for the production of nanocrystals or nanoparticles. These materials can be produced by different methods, using chemical, enzymatic, and physical treatments and may be utilized as drug carriers, quality indicator for food products (nanoencapsulation), and reinforcement biodegradable and nonbiodegradable polymeric matrices [3].

2. Production and characterization methods of starch nanoparticles

The acid hydrolysis is the most commonly adopted method to produce starch nanocrystals (SNC). Usually, the starches submitted to this method have a two-step hydrolysis reaction: in the first step, a fast hydrolysis occurs, and in the second step, a slow hydrolysis occurs. For some authors there are three important steps of the acid hydrolysis: rapid, slow, and very slow [4–6]. In the first stage, the hydrolysis of the amorphous parts of the granules are attacked, while the slow step is the erosion of the crystalline regions [7]. Starch nanocrystals produced for this method present high crystallinity and a platelet-like shape. In this process, starch is diluted in acid (hydrochloric or sulfuric) maintained under constant stirring for a prolonged period with temperature control. After the hydrolysis period, the nanocrystals are differentiated from the acid by centrifugation and washed with distilled water until neutrality of the eluent. Finally, for a homogeneous dispersion of the nanocrystals, the suspension is submitted to a mechanical procedure (ULTRA-TURRAX).

The botanic origin of starch influences the thickness of SNC, which can vary between 4 nm for wheat starch and 8 nm for potato starch and crystalline organization and consequently the size of SNC. This is related to the fact that the acid hydrolysis occurs in the amylose molecules of the starch granules, and depending on the botanic origin of starch, it can be occurred in different sites of granule structure, for example, in the amorphous region (wheat starch), interspersed among amylopectin clusters in both the crystalline and amorphous regions (maize starch), and in bundles between amylopectin clusters or co-crystallized with amylopectin (potato starch) [3]. Thus, depending on the crystalline organization (amylose content), SNC can present larger sizes, since amylose is believed to jam the pathways for hydrolysis. Generally, SNC presents platelet-like morphology.

The lengthy duration of the acid hydrolysis (until 40 days) implies in a low yield (around 5%) [6]. Thus, this method is not appropriate for practical applications due to the long treatment period, its low yield, and use of concentrated acid, which can cause a negative impact on the environment.

The study carried out by Gonçalves et al. [8] using the acid hydrolysis method used to modify the starch extracted from the crude seeds of the pinhão (*Araucaria angustifolia*) was effective,

resulting in nanometric particles. The starch modified by this method showed the greatest differences compared to common starch, being the most soluble, translucent, and hygroscopic among the samples. The authors conclude that the greater solubility and reduced turbidity are interesting from a commercial standpoint, showing that pinhão starch nanoparticles could be useful for the development of coating materials or films. In another study, the method showed an ability to form a strong elastic gel of starch nanocrystals [9]. Some recent studies by production of nanostarch by acid hydrolysis can be observed in **Table 1**.

Gamma radiation (γ -radiation) can be used to develop starch nanoparticles, since this technique can break large molecules into smaller fragments and is capable of cleaving glycosidic linkages. The technique consists in mixing starch and boiling water by stirring it for obtaining a homogenous paste, and then the suspension is irradiated using gamma ray, which generates active free radicals that are then responsible for the hydrolysis of starch. The fragmentation of starch results from the cleavage at the amorphous regions, instead of at the crystallite regions. In this sense, the gamma radiation method is very similar to that of the starch acid hydrolysis. Generally, the diameter of the nanoparticles obtained by this method is below 100 nm. Besides that, these nanoparticles also have nanocrystal aggregates, due to the large number of OH groups on their surface, which becomes strongly associated by hydrogen bonding, leading to fast thermal degradation [14]. The researches involving this method are still scarce and do not report the yield of process, which prevents the comparison with other methods.

Gamma radiation research demonstrates satisfactory results in the characterization and production of starch nanoparticles from cassava and waxy maize; the average sizes determined were (31 ± 5) nm and (41 ± 7) nm, respectively. The study shows that gamma radiation is a successful methodology to obtain starch nanoparticles able to be used as starch reinforcement and as a good alternative to production of starch nanoparticles, with low cost and using a simple and scalable methodology [14]. Gonzales Seligra et al. [28] also obtained average sizes less than 100 nm by producing starch nanoparticles by this same method. The insertion (0.6 wt%) of these nanoparticles in PBAT/TPS films improved the mechanical properties of the blend.

The production of starch nanoparticles (SNPs) using physical treatments is still recent, with high-pressure homogenization and ultrasound treatment being more utilized methods. In these methods, there are no chemical treatments or addition of chemical reagents. Some

Starch source	Time of reaction (days)	Size or size distribution (nm)	Yield (%)	Morphology	Reference
Amaranth	10	376	3.6	Lamellar structure	Sanchez de la Concha et al. [10]
Waxy maize	5	58	—	Platelet	Bel Haaj et al. [11]
Cassava	5	47–178	30	Spherical	Costa et al. [12]
Amadumbe	5	180–280	25	Platelet	Mukurumbira et al. [13]

Table 1. Starch source, time of reaction (days), size or size distribution (nm), yield (%), and morphology found in different studies on obtaining nanostarchs by acid hydrolysis.

advantages of these methods are that they are simple, effective, and environmentally friendly. Besides that, they might reduce the processing time to generate SNPs, increase the yield in NP production, and avoid various purification steps such as the acid hydrolysis [15]. In this context, ultrasound treatment shows up as a viable alternative. The method consists in sonication a starch suspension (starch and water) with controlled temperature for a fixed time, using ultrasound equipment. During the ultrasonication occurs a transfer the energy for to starch particles by cavitation, which is the collapse of microbubbles that burst and propagate as a sound wave through the solution. So microjets are formed with high velocities resulting the shear forces which may break covalent bonds of the starch and reduce the particle size. The ultrasonication process influences the crystalline structure of the starch (amylopectin), leading to nanoparticles with low crystallinity or an amorphous character. The ultrasonication in the starch can be affected by many factors such as ultrasonication power and frequency, time, and treatment temperature, besides the characteristics of starch dispersions, which are the concentration and botanical origin of starch and the dispersion solvent. Thus, the starch nanoparticles obtained for this method also can vary; for example, the size of the nanoparticles may vary between 30 nm and 200 nm. Some studies can be observed in **Table 2**.

The high-pressure homogenization is commonly in the chemical, pharmaceutical, food, and biotechnology industries. In this treatment, changes not only in the products but also in the particles, colloids, or macromolecules which are product constituents may occur. Thus, novel applications for the high-pressure homogenization are researched [17] between the productions of starch nanoparticles. The method consists of the manipulation of a continuous flow of liquid through microfabricated channels; the starch slurry is passed by a microfluidizer, which can be intensified by external pressure sources, external mechanical pumps, integrated mechanical micropumps, or electrokinetic mechanisms, which result in the breakage of the hydrogen bonding inside the large particles by the mechanical shear forces. Homogenization pressures can reach up to 350 MPa. The nanoparticles obtained by this method may vary by 10 nm in size. In this method, the partial or complete destruction of the crystalline structure can also occur, and only a low concentration of starch slurry could be processed for homogenization.

Recently, studies involving the ultrasound treatment and high-pressure homogenization methods show the development of nanoparticles of starch with nanometric scale sizes and the ability to form films [8, 18, 19]. The use of the ultrasound treatment method in pinhão

Starch source	Concentration (wt%)	Power (W)	Size or size distribution (nm)	Morphology	Reference
Waxy maize	2.0	400	40.0	Platelet	Boufi et al. [15]
Cassava	1.5	50	75.51	Spherical	da Silva et al. [16]
Pinhão	20.0	100	454.3	Concave	Gonçalves et al. [8]
Potato	3.0	100	77.0	Spherical	Chang et al. [18]
Waxy maize	1.5	136	100–200	—	Bel Haaj et al. [20]

Table 2. Starch source, concentration (wt%), power (W), and size or size distribution (nm) found in different studies on obtaining nanostarchs by ultrasound treatment.

(*Araucaria angustifolia*) seeds can be useful for the development of novel biocomposites, with improved properties to be employed such as coating materials or films [8]. In other researches, the study not only shows an easily controllable methodology to prepare starch nanoparticles of small size and narrow distribution through precipitation but also provides an approach to produce starch nanoparticles with high efficiency and low cost, decreasing in viscosity of starch aqueous paste and not requiring any chemical treatment [18, 20].

The high-pressure homogenization researches have shown results of starch nanoparticles analyzed by transmission electron microscopy (TEM) and dynamic light scattering (DLS), which showed that starch nanoparticles had narrow size distribution, high dispersibility, and spherical shape [21] and films obtained from high-pressure homogenized dispersions had good moisture barrier capacity, better film transparency, and higher tensile strength but, however, lower elongation [19].

The utilization of the starch nanoparticles as polymeric filler is recent; however, the researchers showed satisfactory results. The nanoparticle presents at least one of its dimensions which is lower than 100 nm; thus, this nanometric dimension may result in a better dispersion and compactness of polymeric structure. The insertion of starch nanoparticle in a polymer results a new material, known as nanocomposite, with great properties that are not seen in traditional composites.

The incorporation of SNPs improves the mechanical properties and water vapor permeability (WVP) and also the biodegradability of the composites. The decrease in the WVP of nanocomposite films is attributed to compactness of the polymeric structure which is resulting in water vapor diffusion more difficult and consequently reducing permeability; in case the reinforcement is derived from the same material as the matrix, such as starch nanocrystals dispersed in starch films, it could have better compatibilization, since they show characteristics inherently from starch granules. It is worth pointing out that the concentration of starch nanoparticle inserted in a matrix polymeric must be carefully analyzed, once a lower nanoparticle concentration leads to better dispersion in the films and less clustering that hinders the passage of water and reduces permeability. On the other hand, the increase in WVP with a higher concentration of the SNPs can be related with a more nanoparticle grouping allowing diffusion of water molecules. Recently, some studies involving the use of SNP as filler in starch films showed that when the concentration of SNPs inserted was less than 6%, the WVP presented a reduction. However, these same studies showed the use of a higher concentration of the SNPs resulting in an increase in WVP [22, 23]. The increase in WVP is not feasible for food packaging use; it offers increased food degradation rate. The WVP values are essential for the possible packaging application use of the biofilms. The material that where very permeable to water vapor may be suitable for the packaging of fresh food, whereas a slightly permeable biofilm may be useful for the packaging of dehydrated food [24].

The mechanical properties are proven be one the most important parameters for biofilm analysis, which usually presented poor mechanical properties. One alternative for improving these properties is the use of starch nanoparticle as reinforcement agent. For the mechanical properties, also the nanometric dimension of the starch nanoparticles can result in strong interactions with different matrices, once they have the capacity of occupying inter- or intramolecular space, resulting in densification of the film [25]. Besides that, the nanoparticle presents high

specific surface area which can result in a better between filler and polymeric matrix interfacial interaction, which result in an increase of the nanocomposite strength [26]. So, the polymeric film incorporated with the SNP can present an increase in the tensile strength and modulus of elasticity, associated with decrease in the elongation percentage. These effects are heavily dependent on the SNP concentrations incorporated in the nanocomposites, because high concentrations of SNPs when incorporated in a matrix can cause aggregation, which leads to weaken the interface adhesion between the nanoparticle and matrix [27]. Li et al. [22] studied the incorporation of starch nanocrystals (SNC) in pea starch films. The authors concluded the concentrations bigger than 5% of SNC when incorporated in the films resulted in a decreased tensile strength associated with increase in elastic modulus.

Besides that, SNPs can speed up the biodegradation process. The influence of the SNP in the faster biodegradability of the composites is due to the fact that in soil, water diffuses into the polymer sample, causing swelling and enhancing biodegradation due to increases in microbial growths [28]. Costa et al. [12] studied the use of cassava starch nanocrystals (CSN) obtained by acid hydrolysis to strengthen nanocomposite films from the same matrix. The authors conclude that the large percentage of loss of film mass was found over the biodegradability test and the film with 10% CSN showed a larger weight loss, which is probably associated with greater microorganism access.

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Conflict of interest

The authors declare no conflicts of interest.

Author details

Normane Mirele Chaves Da Silva¹, Fernando Freitas de Lima², Rosana Lopes Lima Fialho¹, Elaine Christine de Magalhães Cabral Albuquerque¹, José Ignacio Velasco³ and Farayde Matta Fakhouri^{3,4*}

*Address all correspondence to: farayde@gmail.com

1 Polytechnic School, Federal University of Bahia, Salvador, BA, Brazil

2 School of Chemical Engineering, University of Campinas, Campinas, SP, Brazil

3 ESEIAAT, Universitat Politècnica de Catalunya - Barcelona TECH, Barcelona, Spain

4 Faculty of Engineering, Federal University of Grande Dourados, Dourados, MS, Brazil

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