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Development and characterization of starch nanoparticles by gamma radiation: Potential application as starch matrix filler

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ABSTRACT

Gamma radiation arises as an advantageous alternative to obtain starch nanoparticles given its low cost, simple methodology and scalability. Starch nanoparticles (SNP) with sizes around 20 and 30 nm were obtained applying a dose of 20 kGy from cassava (CNP-γ) and waxy maize (WNP-γ) starch, respectively. They showed the same thermal degradation behavior and their maximum mass loss zone was similar to those nanoparticles obtained from acid hydrolysis (WNP-h). Additionally, CNP-γ and WNP-γ were used as nanofillers in a cassava matrix. Increments of 102% in storage modulus were obtained with the addition of only 2.5 wt.% of WNP-γ, showing that gamma radiation is a successful methodology to obtain SNP able to be used as starch reinforcement.

1. Introduction

Starch has received considerable attention during the past decades as a biodegradable thermoplastic polymer and as biodegradable particulate filler. The main advantages of starch fillers are: their renewable nature; availability; high specific strength; non-abrasive nature that allows easier processing even at high filling levels; biodegradability; and a relatively reactive surface which can be modified by adding reactive groups compatible with the polymeric matrix (García et al., 2012; Le Corre, Bras, & Dufresne, 2010). It is well known that it is possible to obtain starch nanoparticles (SNP) by starch acid hydrolysis (García, Ribba, Dufresne, Aranguren, & Goyanes, 2009). These nanoparticles were used to reinforce different kinds of matrices, such us starch (García, Ribba, Dufresne, Aranguren, & Goyanes, 2011), PVA (Sreekumar, Al-Harthi, & De, 2012), and synthetic latex (Dufresne & Cavaille, 1998). As a consequence of the particle nanometric size, their addition in very small amounts produces significant improvements in the mechanical and permeation properties of different matrices (Duquesne, Habibi, & Dufresne, 2012; García et al., 2011; Labet, Thielemans, & Dufresne, 2007; Piyada, Waranyou, & Thawien, 2013). In particular, the incorporation of SNP in starch matrices led to improvements in elastic modulus and water vapor resistance (Behera, Avancha, Sen, & Adhikari, 2013; García et al., 2009).

Starch consists of mainly two glucosidic macromolecules: amylose and amylopectin. According to Jenkins et al. (1994), the crystallinity of starch granule is associated with the amylopectin component. Besides, the authors proposed a model considering the shells to be formed by alternating crystalline–amorphous layers. It is noteworthy that the amylopectin content depends on the botanic origin.

Gamma radiation (γ-radiation) can be a convenient tool for modification of polymer materials through cross-linking, grafting and degradation techniques. It has also been suggested as a rapid and convenient modification technique which breaks large molecules into smaller fragments and is capable of cleaving glycosidic linkages (Singh, Singh, Ezekiel, & Kaur, 2011). Gamma radiation may generate free radicals on starch molecules which are capable of hydrolyzing chemical bonds, thereby cleaving large molecules of starch into smaller fragments of dextrin (Yu & Wang, 2007). In particular, it is expected that α-D-(1–4)-glycoside linkages are the most susceptible bonds to be cleaved by γ-radiation. Bao, Ao, and Jane (2005) investigated how gamma radiation affects the structures and physical properties of starch in order to understand the mechanisms which affect starch granule structures. They concluded that fragmentation mostly resulted from the cleavage at the amorphous regions, instead of crystallite regions, but little changes in the amylopectin branch chain length occurred. This mechanism was similar to that of the starch acid hydrolysis (Bank,

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Greenwood, & Muir, 1973; Hoover, 2000). It is important to mention that although free radicals could be involved in the mechanism they easily recombine in water, thus solutions obtained from gamma irradiated samples are radical free.

Akhavan and Ataeevarjovi (2012) have recently showed that gamma radiation would be an effective protocol in the size reduction of particles based on soluble starch. The mean size of these particles could be changed by the use of surfactants during the formation process under gamma irradiation. On the contrary, γ-irradiated solid starch samples have produced different results, as reported by Singh et al. (2011). In that research, it was observed that the intensity of XRD peaks decreased by increasing the irradiation dose for potato starch from two different cultivars. They employed gamma radiation from 0.01 to 0.5 kGy and concluded that starch irradiated at 0.5 kGy did not show presence of any organized crystalline structure. However, Bao et al. (2005) studied physical and structural characteristics of rice flour and starch obtained from gamma irradiated white rice at different doses between 0.5 and 9.0 kGy. These authors showed that the crystallinity increased in irradiated starch. The shape and size of starch particles depend strongly on its botanic origin. Then, the kind of native starch and the processing technique determine the starch properties after irradiation process.

The aim of this work is to develop starch nanoparticles applying gamma radiation, since this technique is commonly employed for food industries and would allow the SNP mass production with low costs. The influence of amylopectin content in the morphology, structure and thermal response was studied employing two different kinds of starch: native cassava and native waxy maize. The gamma radiation was carried out in both starch water dispersions. In order to compare the properties of SNP from waxy maize starch obtained by this novel procedure with one of the traditional methods, acid hydrolysis was also carried out.

Finally, the possibility of using the nanoparticles that have been obtained applying gamma radiation as starch matrix nanofiller was also studied.

2. Experimental

2.1. Materials

The native cassava starch (CS) (72 wt.% amylopectin and 28 wt.% amylose) was provided by Bernesa S.A., Buenos Aires, Argentina. The native waxy maize starch (WS) (99 wt.% amylopectin) was provided by Roquette S.A., Lestrem, France. The starches are native. None of these starches have received any physical or chemical modification. It was provided as supplementary data scanning electron micrographs for both starch types. The average size of cassava starch granule was 10 μm with a standard dispersion of $\sigma = 3$ μm. In the case of waxy maize starch granule the average size was 11 μm with a standard dispersion of $\sigma = 4$ μm.

2.2. Starch nanoparticles obtained by acid hydrolysis

In order to compare nanoparticles obtained by gamma radiation with the ones obtained by the traditional methodology, waxy maize nanoparticles were obtained by acid hydrolysis as previously reported (García et al., 2009). We employed 36.725 g of waxy maize starch and then mixed in 250 mL of 3.16×10^{-3} M H_2SO_4, at 40 °C and 100 rpm, subjected to an orbital shaking action for 5 days. After that, crystals were washed in distilled water and separated by successive centrifugations until neutrality was reached. They were lyophilized and the powders obtained were named WNP-h.

2.3. Starch nanoparticles obtained by gamma irradiation

In order to prepare the samples to be treated by gamma radiation, starch stable dispersions were prepared according to the well known process (Vogel, 1983, chap. IX): 5 g of starch were mixed with 5 mL of distilled water at room temperature using a mechanic stirring at 180 rpm obtaining an homogenous paste. After that, this paste was quantitatively transferred to a 500 mL glass beaker. Then 495 mL of distilled water at 85 °C were added with magnetic stirring for 30 s. Immediately, the beaker was cooled at 5 °C and stored at room temperature in a hermetic vessel. This procedure let us to achieve cassava and waxy stable dispersions (CSD and WSD) for at least 1 month, without employing any other additives.

After obtaining these stable dispersions, samples were irradiated with 20 kGy using ^{60}Co gamma-ray source facility of the Ezeiza Atomic Center-Argentina. The irradiation was developed at room temperature with an irradiation rate of 14 kGy/h. Both irradiated and non-irradiated samples were lyophilized. The obtained powders for the non irradiated stable dispersions were named CPD (cassava powders from stable dispersion) and WPD (waxy powders from stable dispersion). On the other hand, the powders obtained after gamma irradiation and lyophilization were named CNP-γ and WNP-γ for cassava and waxy starch, respectively.

2.4. Preparation of plasticized starch films

Thermoplastic starch was processed by casting as previously reported (García et al., 2009) from the mixing of native cassava-starch granules, glycerol and distilled water. A quantity of 15 g of a starch/glycerol mixture (3:1 by weight) was dispersed in 179 g of distilled water. The mixture was heated from room temperature at a heating rate of 1.59 °C/min under magnetic stirring for 28 min until gelatinization, which occurred at 70 °C. After gelatinization, the gel was degassed for 10 min with a vacuum mechanical pump. At that point, the composite films were prepared by adding the suspension of both starch nanoparticles (CNP-γ and WNP-γ) in the desired quantities (2.5 wt.% relative to the total mass). After that, the mixture was stirred for 10 min at 250 rpm and degassed for another 5 min. Then, the mixture was cast in a plastic mould and evaporated in a ventilated oven at 50 °C for 48 h. Solid films having a thickness between 300 and 400 μm were obtained. Matrix and composite films were stored at 43% relative humidity (RH) (K_2CO_3 saturated solution) for 2 weeks before characterization. In order to study the modifications due to the incorporation of starch nanoparticles, matrix films were also developed by using the same methodology.

2.5. Characterization

2.5.1. Field emission scanning electron microscopy (FE-SEM)

Field emission scanning electron microscopy (FE-SEM) was performed using a Zeiss DSM982 Gemini with a field emission gun (FEG), to examine the morphology of starch nanoparticles. All the samples were observed with an acceleration voltage of 5 kV.

Samples obtained after gamma irradiation were observed using two different sample deposition methodologies. For the first one we employed dispersions in deionized water of lyophilized samples (CNP-γ and WNP-γ). Drops of these dispersions were put onto silicon waffer and dried in vacuum during 24 h. For the second methodology, lyophilized samples were sprinkled onto a carbon tape. The same processes were employed to study nanoparticles obtained by acid hydrolysis methodology (WNP-h).

Cryogenic fracture surfaces of plasticized starch films (matrix and matrix with each SNP) were observed using field emission scanning electron microscopy (FE-SEM).