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Potential of taro starch spherical aggregates as wall material for spray drying microencapsulation: Functional, physical and thermal properties

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ABSTRACT

Taro starch spherical aggregates have been considered as wall material for the microencapsulation of bioactive compounds. The distribution of particle size, morphology, stability, glass transition temperature, ζ-potential, physical properties and flowability and compression indexes, and functional properties (water, oil and dye retention capacity) were measured. The average diameter was 17.5 ± 0.3 μm. Aggregates formed by a relatively high number of starch granules were observed. The residual protein in the aggregates was in the periphery of the starch granules, favoring the aggregation and the stability under aqueous stirring conditions. The ζ-potential was −21.8 ± 0.3 mV. The value of the glass transition temperature was in the range from 176.8 to 75.4 °C, with 5% and excess water, respectively. The Hausner ratio and Carr index were 1.06 and 14.7, respectively. The oil holding capacity was 1.2 ± 0.01 g of oil·g^{-1} of dry solid. Overall, the functional, physical and thermal properties of the spherical aggregates of taro starch granules showed that this material offers good potential for the microencapsulation of bioactive compounds.

1. Introduction

Starch spherical aggregates with small granule size (diameter <10 μm) are viable structures for the micro-encapsulation of bioactive compounds [1]. The formation of spherical aggregates requires stability of starch granules and the action of a bonding agent. The mechanism involved in the formation of spherical aggregates is not clear at all, although some results in the literature pointed out to the formation of complexes between positively charged proteins located on the granule surface and negatively charged polysaccharides. In an interesting study, Debet and Gidley [2] showed that proteins play a central role in the integrity of insoluble remnants after gelatinization of starch dispersions. In fact, proteins play the role of a bonding agent for maintaining the cohesion of starch granules. It can be postulated that similar mechanisms could be involved in the formation of spherical aggregates. However, in many cases the fraction of proteins does not suffice to stabilize the structure of spherical aggregates, such that an external bonding agent (e.g., gum Arabic, carboxymethyl cellulose and carrageenan) should be added. Taro starch is an interesting case where the fraction and possibly the nature of proteins lead to the formation and stabilization of spherical aggregates. Gonzalez-Soto et al. [3] reported that taro starch has the ability of forming spherical aggregates without the addition of bonding agents. In fact, isolated taro starch contains a relatively high content of protein (5–7%), which suffices for bonding starch granules within a spherical configuration. The characterization of taro starch spherical aggregates focused on the study of the changes within the internal structure of the starch granules influenced by the spray drying process and the effect of the binding agents addition at different ratios [2–4]. However, other characteristics such as the glass transition temperature, the stability under water and stirring conditions, the ζ-potential, physical and functional properties remain scarcely explored. These characteristics provide valuable information for assessing the potential of taro starch spherical aggregates to obtain a stable wall material and for the protection of a core material.

The characteristics of the wall material, such as chemical structure, thickness, pore size and surface integrity, play a determining role in the transport and release properties of the core material and on the stability of the microcapsules. It is well-known that the diffusion through a material is facilitated by the rubbery state, while in the vitreous state the diffusion is relatively slow [6]. The plasticizing effect on the wall material induced by the glass transition can cause the ordering or rupture of the polymer structure, resulting in undesirable changes of the characteristics of a microencapsulant matrix [7]. Commonly, the glass transition temperature is estimated by calorimetric techniques. In the modulated differential scanning calorimetry (MDSC), the sample undergoes a sinusoidal oscillation of the temperature superimposed on a heating ramp of the conventional calorimetry, so that the total heat flow can be separated in its heat capacity (reversible heat flow) and kinetic components (irreversible heat flow) [8,9]. On the other hand, the

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production of microcapsules involves in general high shear and elongation conditions with significant temperature gradients. Mechanical forces and temperature gradients in food processing equipment could induce substantial deformations of a microcapsule, leading to rupture of the wall material and premature release of the core material [10]. Stability of microcapsules under stringent stirring conditions is an issue that has been rarely addressed.

The objective of this study was to assess the characteristics of taro starch spherical aggregates, such as the size and morphology, stability under agitation in aqueous medium, ζ-potential, glass transition temperature, bulk density, absolute density, particle density, apparent porosity, flowability and compressibility indexes, and some functional properties (water, oil and dye retention capacity). These characteristics would provide valuable insights in the ability of taro starch spherical aggregates for providing protection to bioactive compounds, as well as for estimating optimal process conditions for the application of spherical aggregates.

2. Materials and methods

2.1. Preparation of spherical aggregates

Taro flour was produced from collected corms of *Colocassia esculenta* var. Esculenta harvested in a commercial crop at Tuxtepec, Mexico. Starch isolation was carried out following the Whistler patent [11] procedure. The starch was filtered through 50, 100 and 325 US mesh. After the final washed of starch, the solid concentration of the starch slurry was adjusted to 30 g · 100 g^{-1} water. The starch dispersion was fed to a Mini Spray Dryer (Model B-290, BÜCHI UK Ltd., Chadderton, UK) equipped with a double flow atomizer. The drying conditions were the previous reported by Gonzalez-Soto et al. [3], with inlet temperature 145 °C, outlet temperature 80 °C and flow rate of 7.6 g·min^{-1}. The dried powder was stored in a glass container to further analysis. Before spray drying, a fraction of starch slurry was centrifuged at 10,800*g* for 15 min, and the precipitated starch paste was transfer to a forced convection oven (40 °C, 24 h) to obtain native taro starch conventional dried [12]. This sample was used for comparison purposes.

2.2. Preparation of taro starch spherical aggregates-low protein content

Conventionally dried native taro starch (3.0 g) was dispersed in 25 mL NaOH (0.2 g · 100 mL^{-1}). The dispersion was magnetic stirred for 2 h. After stirring, the dispersion was centrifuged (5000*g* for 5 min), the supernatant was discarded and the precipitated was washed with water until achieved pH ~7. An aqueous dispersion (30 g · 100 g^{-1}) was prepared with the precipitated starch and was spray dried under some conditions used to taro starch spherical aggregates preparation.

2.3. Water activity, moisture, protein and starch content

Moisture and protein content were tested following the AACC methods 44-15.02 and 45-13.01, respectively [13]. Total starch was determined by means of the total starch kit procedure from Megazyme International Ireland Ltd., using the Item C for samples containing resistant starch. Water activity was tested in a pa_w kit instrument (Decagon Devices, Inc., Pullman, Washington, US).

2.4. Particle size distribution and morphology

The size distribution of spherical aggregates was measured using a Mastersizer 3000 instrument (Malvern Instruments Ltd., Malvern, Worcestershire, UK) equipped with a Hydro EV accessory. The sample was diluted in water until 12–15% laser obscuration. The sample measure time was 15 s without sonication. The sample was analyzed by triplicate. The morphology of the starch spherical aggregates was observed with a JSM 5600LV microscopy (JEOL, Tokyo, JP), the resolution was 5 nm in low vacuum (LV) mode. The instrument conditions were 20 kV electron acceleration voltage, 12–20 Pa of pressure, and the images were obtained from backscattering electron signal. Additionally, taro starch spherical aggregates were observed in a confocal laser scanning microscope (LSM 710 NLO, Carl Zeiss Microscopy GmbH, Jena, DE) in stack mode, filters 417–729, laser at 405 nm (50.0%), 561 nm (6.5%), 468 (7.5%) and 633 nm (8.0%). Previous scanner was done to test the autofluorescence region of protein fraction.

2.5. Stability under stirring conditions

Stirring operations are typically observed in the food industry. The encapsulated biocompounds added to a food product should resist the conditions of mixing or homogenizing. The stability of spherical aggregates was tested following the Zhao and Whistler [1] procedure. Briefly, a sample of spherical aggregates was dispersed in water (5 g · 100 g^{-1}) at 25 °C by stirring at 100 rpm for 24 h. The shear-rate conditions were about 1.8 s^{-1} with Reynolds number for cylindrical tanks of the order of 12. An axial impeller was used for inducing turbulent flows with both elongational and rotational shear effects. Aliquots were takes each hour and analyzed in the Mastersizer 3000 instrument under the same conditions used for particle size distribution analysis.

2.6. ζ-Potential

The surface charge was measured as ζ-potential. The ζ-potentials of spherical aggregates and native taro starch (oven dried) were assessed in a Zetasizer Nano Z instrument (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The measurement was replicated three times.

2.7. Glass transition temperature

The evaluation of the effect of relative humidity (RH) on the glass transition temperature was evaluated. To this end, taro starch spherical aggregates were exposed to a different relative humidity conditions in desiccators containing saturated salt solutions. The values of the RH were 13% (LiCl), 26% ($MgCl_2$), 46% (K_2CO_3), 57% (NaBr) and 72% (NaCl) at 26 °C. The samples were stored under those RH conditions for 2 weeks. The moisture was assessed to assure the water content in the sample. The glass transition temperature of taro starch spherical aggregates in water excess and RH conditioned was assessed by modulated temperature differential scanning calorimetry (MTDSC) using a DSC instrument (TA Instrument, Q20, New Castle, NJ, US) in modulated temperature setting. For analysis under water excess, the sample (2.2 mg d.b) was weighted in aluminum pan with 80% (w/w) of deionized water. The temperature profile consisted in two heating from 10 to 110 °C, 2 °C·min^{-1} heating rate, modulation conditions amplitude 0.5 °C and frequency of 60 s. For RH conditioned, 5 mg of sample was weighted and the heating rate of MTDSC was 5 °C·min^{-1}. The samples were run by triplicated. The analysis of the glass temperature (T_g) was made directly from the instrument software. The reversible heat flow was used to the analysis.

2.8. Density, apparent porosity, flowability and compressibility index

The physical properties were measured for native taro starch, taro starch spherical aggregates and native maize starch. The latter sample was used as reference material since the physical properties of maize starch has been widely studied. The bulk density (d_b) was determined from 3 g of taro starch spherical aggregates weighted in a 25 mL volumetric graduated cylinder. The occupied volume by the sample was registered. The particle density (d_p) was tested with the previous weighted sample, which was mechanically taped until constant volume. The