Ultrasonics - Sonochemistry 42 (2018) 795–804

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Microstructural and techno-functional properties of cassava starch modified by ultrasound

Yuliana Monroy[a], Sandra Rivero[a,b], María A. García[a,b,*]

[a] CIDCA (Centro de Investigación y Desarrollo en Criotecnología de Alimentos), 47 y 116 S/N, La Plata (B1900AJJ), Buenos Aires, Argentina – Centro Científico Tecnológico La Plata (CCT-La Plata) CONICET, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), Argentina
[b] Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), Argentina

ARTICLE INFO

Keywords:
Physical modified starch
SEM and CLSM observations
Structural analysis
Rheological behavior

ABSTRACT

This work was focused on the correlation between the structural and techno-functional properties of ultrasound treated cassava starch for the preparation of tailor-made starch-based ingredients and derivatives. Furthermore, the effect of treatment time, sample conditioning and ultrasound amplitude was studied. Ultrasonic treatment of cassava starch induced structural disorganization and microstructural changes evidenced mainly in the morphological characteristics of the granules and in their degrees of crystallinity. These structural modifications were supported by ATR-FTIR and SEM and CSLM studies as well as DRX and thermal analysis. The selection of the processing conditions is critical due to the complete gelatinization of the starch was produced with the maximum amplitude tested and without temperature control. Rheological dynamical analysis indicated changes at the molecular level in starch granules due to the ultrasound treated, revealing the paste stability under refrigeration condition. PCA allow to establish the interrelationships between microstructural and techno-functional properties. In summary, different starch derivatives could be obtained by adjusting the ultrasound treatment conditions depending on their potential applications.

1. Introduction

Starch-based derivatives are nowadays used for many applications in food processing in order to achieve particular technological properties. In this way, the native starch granules can be modified by applying physical, chemical or enzymatic modifications. Starch modifications promote molecular disorganization, polymer degradation, molecular rearrangement, polymer crosslinking, and oxidation or addition of chemical groups [1,2]. Through these modifications, starch derivatives are obtained and characterized in order to explore their functionality and versatility [3].

According to Wurzburg [4] and Singh et al. [1], the chemical modification of starches involves etherification, esterification, crosslinking and grafting reactions that allow the introduction of functional groups in the starch chains, or decomposition reactions (acid or enzymatic hydrolysis and oxidation). Pedrosa Silva Clerici [5] has proposed different conventional methods of modification, its use for the production of thermoplastic starch by extrusion and other potential uses. In this sense, Pérez-Sira and González-Parada [6] have modified starches by a combination of pregelatinization and extrusion. Currently, there is a wide range of modified starches on the market, mainly destined to the food, pharmaceutical, paper and textile industries, most of them from maize, potatoes and wheat. The physical modification of cassava starch and the study on their functional properties have hardly been reported and requires a deep analysis.

According to official data, a growth of the modified starch market is expected to reach 4.1% during 2017 and it is projected to achieve USD 12.14 billion up to 2022 [7], indicating the high demand for this type of ingredients. However, the highest proportion of the products marketed correspond to chemically modified starches involving the use of toxic substances and non-environmentally friendly procedures regarding the waste that they generate and the energy consumption involved. In this sense, one of the most widely used modified starch requires the use of crosslinking agents such as phosphorus oxychloride and epichlorohydrin, which are recognized by their toxicity [8,9].

The ultrasound is the sound waves at a frequency which exceeding the audible threshold of the human hearing range. Ultrasound treatment (UT), is a physical method of starch modification that has shown many advantages in terms of higher selectivity and quality, reduced use of chemicals and processing time, and finally serving as an environment-friendly processing [10]. The effects of UT results from acoustic cavitation, which is the fast generation, growth, and finally implosive

* Corresponding author at: CIDCA (Centro de Investigación y Desarrollo en Criotecnología de Alimentos), 47 y 116 S/N, La Plata (B1900AJJ), Buenos Aires, Argentina – Centro Científico Tecnológico La Plata (CCT-La Plata) CONICET, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), Argentina
E-mail address: magarcia@quimica.unlp.edu.ar (M.A. García).

https://doi.org/10.1016/j.ultsonch.2017.12.048
Received 13 November 2017; Received in revised form 26 December 2017; Accepted 27 December 2017
Available online 27 December 2017
1350-4177/ © 2017 Published by Elsevier B.V.

collapse of bubbles in liquid that generates heat (up to 5000 K) and pressure (up to 20 MPa) just in a short time [11]. During UT, ultrasound energy can be transferred to starch granules through a process called cavitation, which refers to the formation, growth, and rapid collapse of microbubbles [12]. As a result of this treatment, the polymer chains near the collapsing microbubbles are caught in a high gradient shear field, which leads to the breakage of macromolecular C—C bonds, and formation of long-chain radicals [13].

To the best of our knowledge, scarce studies that make a comprehensive analysis of the microstructural changes and its relationship with the functional properties of cassava starch modified with ultrasound are reported. Moreover, published data are centered mainly on the effect of UT on the physical properties and the changes experienced in corn, potato, and rice starch properties.

This work was focused on the correlation between the structural and techno-functional properties of physically modified cassava starch (*Manihot esculenta*), as a contribution to the application of ultrasound treatment, a simple and environment-friendly approach for the preparation of tailor-made cassava starch-based derivatives.

2. Materials and methods

2.1. Cassava starch ultrasound treatment

Cassava starch was provided by the Cooperativa Agrícola Mixta de Montecarlo (Misiones, Argentina), containing 17% amylose. Aqueous cassava starch suspensions at a concentration of 5% (w/v) were treated with ultrasound at a power of 750 W and 40% amplitude during different times (5, 10 and 20 min) in a Sonics VCX-750 ultrasonic equipment (Vibra Cell, USA). Additionally, the condition of 60% for 20 min was also analyzed in order to study the ultrasound amplitude influence. Two conditions were assayed: with or without cooling down during sonication by immersion in an iced-water bath of the sample container, considering that, as it is well known, the ultrasound application raises the temperature of treated samples. Table 1 shows the processing conditions and the nomenclature used in each case. Samples were centrifuged at 2500 rpm for 10 min and dried in an oven at 37 °C up to a constant weight in order to obtain the modified starches, which were then ground in a mortar until a fine powder was obtained, which was sieved through a sieve of 53 µm (ALEIN International, Argentina).

2.2. Structural studies of modified cassava starches

2.2.1. Microscopic analysis: SEM and CLSM

Starch granule morphology was analyzed by SEM using a low vacuum FEI model Quanta 200 scanning electron microscope (Eindhoven, The Netherlands). Starch samples were mounted on bronze stubs with a double-sided adhesive tape and then coated with a thin gold layer. Samples were examined at an acceleration voltage of 20 kV.

Likewise, confocal Laser Scanning Microscopy (CLSM) was used to complement the starch granule morphology studies. All samples were examined after binding with fluorescein isothiocyanate (FITC), a fluorescent label freshly prepared in 0.3 mg/mL pH 9 buffer ($NaHCO_3$ 50 mM and NaCl 100 mM). Native and modified starches (5 mg/mL) were suspended in milli-Q water and 1000 µL of the suspensions were stained by the addition of 40 µL of FITC. Starch granules were visualized using a LEICA TCS SP5 (Mannheim, Germany) inverted microscope equipped with an Ar laser, at excitation and emission wavelengths of 488 and 518 nm, respectively. Images were acquired using a HCX PL APO CS63.0 × 1.40/UV/oil immersion objective with 1024 × 1024 pixel resolution, in a constant z-position. Software Leica Application Suite Advanced Fluorescence (LAS AF), version 2.2.1. build 4842 was employed in the image analysis.

2.2.2. Granule size distribution

The size of the starch granules was determined (expressed in % volume) was determined by Dynamic Light Scattering (DLS) with a particle size analyzer (Malvern Mastersizer 2000E, Malvern Instruments Ltd., Worcestershire, U.K.). Measurements were performed in quadruplicate at room temperature. The refractive indices of 1.33 for water and 1.52 for starch were used as standards according to Torres et.al [14].

2.2.3. ATR-FTIR

Molecular interactions study was carried out by means of ATR-FTIR technique. Spectra were recorded using a Nicolet, iS10 Thermo Scientific (Madison, USA) by the accumulation of 32 scans at 4 cm^{-1} resolution in the 4000–400 cm^{-1} wavenumber range. Starch powders were placed onto a diamond ATR crystal using a top-plate and pressure-arm accessories (Smart iTX accessory) for the Nicolet™ iS™10 (Thermo Scientific™, Madison, USA). Data were analyzed by using the software Omnic 8 (Thermo Scientific, Madison, USA).

The spectral deconvolution of the peaks within the region 1065–950 cm^{-1} was performed by using curve fitting algorithms. Inverted second derivative spectra were used to estimate the number, position and relative contribution of individual components.

The software iterated the curve-fitting process by adjusting the high and width of the peaks to achieve the best Gaussian-shaped curves that fit the original spectrum.

2.2.4. X Ray diffraction

The characteristic patterns of native and modified cassava starch were evaluated by X-ray diffraction in a X'Pert Pro Analytical Model PW3040/60 (Almelo, The Netherlands). The CuKα radiation (1.542 Å) was generated at 30 mA and 40 kV, recording the relative intensity in the scattering range of (2θ) 3–60° with a step size of 2θ = 0.02°. The relative crystallinity was determined as the ratio of the crystalline area to the total area by using the Origin software (Version 7.0, Microcal Inc., Northampton, MA, USA) and expressed as (%) [3].

2.3. UT modified cassava starch characterization

2.3.1. Differential scanning calorimetry (DSC)

Thermal properties of native and modified starches were conducted by using a DSC model Q100 controlled by a TA 5000 module (TA Instruments, New Castle, Delaware, USA), with a quench cooling accessory, under a N_2 atmosphere (20 mL min^{-1}). Samples were analyzed between 10 °C and 120 °C, at a heating rate of 10 °C/min.

About 10 mg of 20% (w/w) aqueous suspensions of native or modified starch were weighed in preweighed aluminum pans which were hermetically sealed. An empty pan was used as reference. From

Table 1
Nomenclature used and temperatures reached for cassava starch granules modified under different ultrasound conditions.

	Conditions		Nomenclature	Process temperature (°C)	
	Amplitude	Time (min)		Initial	Final
Native			N		
Without ice bath condition	40%	5	U5	22	33
		10	U10	22	40
		20	U20	22	50
With ice bath condition	40%	5	UB5	22	21
		10	UB10	22	28
		20	UB20	22	37
Without ice bath condition	60%	20	U 60%	22	65
With ice bath condition			UB 60%	22	24

Download English Version:

https://daneshyari.com/en/article/7703445

Download Persian Version:

https://daneshyari.com/article/7703445

Daneshyari.com