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Modeling process conditions of modified starches to be used as wall materials in the encapsulation by nano-spray drying

Modelación de las condiciones de modificación de almidones para utilizarse como materiales de pared en la nano-encapsulación mediante secado por aspersión

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Abstract

In the present work, time-variable modeling of high-energy mechanical grinding (0, 20, 30, 40, 50, 60, 70, and 80 min), was carried out to obtain the best grinding conditions process for obtaining modified starches with applications as wall materials with favorable viscosity and particle size characteristics for the nano-encapsulation of bioactive compounds by means of nano-spray drying. The pasting profile was affected by the different mechanical grinding times, since the maximum viscosity (95 ºC) decreased as the grinding time increased, but this was not the case in the cooling stage (30 ºC) since at times of 30 and 40 min the viscosity was more significant than the maximum viscosity. The modified starches showed larger particle sizes compared to their native counterpart, indicating the formation of agglomerations. The model presents an adequate fit with respect to the experimental data and the feasible and infeasible conditions of this process are represented.

Keywords: Nano-spray, Starch modified, Wall materials, Nano-encapsulation, Modeling.

Resumen

En el presente trabajo se realizó una modelación de la variable tiempo de la molienda mecánica de alta energía (0, 20, 30, 40, 50, 60, 70 y 80 min), para determinar las condiciones que permitan obtener almidones modificados con características de viscosidad, y tamaño de partícula, que potencialicen su uso como materiales de pared en la nano-encapsulación de compuestos bioactivos mediante secado por aspersión. El perfil de empastado fue afectado por los diferentes tiempos de molienda: la viscosidad máxima (95 ºC) disminuyó a medida que aumentó el tiempo de molienda, sin embargo, en la etapa de enfriamiento (30 ºC) la viscosidad fue mayor que la viscosidad máxima a los 30 y 40 min. Los almidones modificados mostraron tamaños de partículas más grandes en comparación con su contraparte nativa, lo cual indica la formación de aglomeraciones. El modelo presenta un ajuste adecuado con respecto a los datos experimentales y se representan las condiciones factibles y no factibles de este proceso.

Palabras clave: nano-secado por aspersión, almidón modificado, material de pared, nano-encapsulación, modelación.

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1 Introduction

Chayote is a perennial herbaceous, monoecious (both sexes), climbing plant, native to Mexico and Central America (Lira, 1996). This tuberized root is an attractive option for agronomy because it contains starch as itsmain component and can be used as an alternative source for its isolation, however, there is limitedinformation on the starch of the chayote tuberized root. Hernández-Uribe *et al*., (2011) isolated and physicochemically and rheologically characterized chayotextle starch grown in Hidalgo, Mexico. They reported a 49% yield, with a starch purity of 89%. The physicochemical properties showed an amylos econtent of 26.3%, with a type B diffraction pattern, with a high peak viscosity and a low gelatinization temperature compared to potato starch. They presented viscoelastic properties with elastic predominance, with the modulus G' greater than G". The yield and purity, as well as the physicochemical and rheological properties are of importance for industrial applications, hence the interest in the extraction and characterization process for its use as a food additive, a food packaging material, and a wall material for encapsulation. Starch is a polysaccharide widely used in the food industry as ingredients for the manufacture of various products, such as soups, cookies, snacks, cereals (Huang *et al.,* 2021), due to its functional and physicochemical properties that it presents as a thickener, capacity expansion, solubility, pasting, gelatinization temperature (Chen *et al.,* 2010),

In recent years, other applications that have drawn attention to the starch industry have been directed to its use as wall material in the encapsulation of bioactive compounds (antioxidants, oils, vitamins) by spray drying (Alias *et al.,* 2021). Spray drying is a widely used technique to protect bioactive compounds from various degradation reactions (Hoyos-Leyva *et al.,* 2018). Various authors have used starches from various sources as wall material for the encapsulation of bioactive compounds. Encapsulated compounds are introduced in a matrix with the aim of preventing their loss, reducing their instability by protecting them from external factors and prolonging the shelf life of the products (Mukurumbira *et al.,* 2022). In addition, it allows promoting easy handling, controlling the release during the moment of its application and improve the sensory and/or functional properties of the products in which they are applied (Baranauskiené *et al.,* 2006). The efficiency of encapsulation and the stability of the capsules during storage depends mainly on the composition of the wall material (Gharsallaoui *et al.,* 2007). Generally, the criteria for selecting wall materials are based on good physicochemical properties such as film-forming, high solubility, low viscosity at high concentrations, emulsification, melting/glass transition temperature, crystallinity, and low cost. In its native form, starch presents limitations for its application due to its intrinsic properties such as low resistance to shear and thermal decomposition, high retrogradation and synthesis, as well as low solubility in common organic solvents. So, for application-specific purposes, it is necessary to modify the properties through various methods. The modification of the starch expands its versatility and provides desirable functional attributes, which allows it to offer an economical alternative to other hydrocolloid components that are of low availability and high cost (Tharanathan 2005; Neelam *et al.,* 2012). Techniques for starch modification have been classified into four categories: physical, chemical, biochemical and genetic modifications, or a combination of these.

One of the most recent trends in encapsulation of bioactive food ingredients is nanoencapsulation, which typically involves nanocarriers with dimensions smaller than 100 - 1000 nm. Another obstacle is the production of very small droplets; ultrasonic atomizer based on a vibrating mesh technology can produce these tiny droplets forconversion into nanoparticles, but low viscosities in the feed mixture are required (Assadpour and Jafari, 2019; Vázquez-León *et al*., 2022). For example, the nano spraydryer B-90 development by Büchi Company requires nanocarriers with particle size $<7\ \mu$m and viscosities $\leq$0.01 Pa·s in the feed mixtures, to carry out the dried process. Thus, researchers need carry out a modification of native starch to produce starch-based nanocarriers that comply with these technical specifications, and the physical treatments can be an option.

Physical treatments generally produce changes only in the packing arrangements of the starch polymer molecules within the granules, such changes can have a significant impact on the properties of the starch, the attributes of its pastes and gels, and even its digestibility. These modifications are of interest since they do not imply any chemical treatment that could be harmful for human consumption. Recently, high-energy mechanical grinding has been used as an alternative physical modification to conventional chemical modification methods (Moraes *et al.,* 2013;

Zhang *et al.,* 2012; Lin *et al.,* 2016; Liu *et al.,* 2018; Huang *et al.,* 2021; Juarez-Arellano *et al.,* 2021; Chorfa *et al.,* 2022).

When mechanical grinding is used on starch, the effects of friction, collision, shear and other mechanical actions modify the starch granule size and the crystalline structure and, consequently, the physicochemical properties of the starch granules, which produces gradual changes in the molecular structure, the crystalline structure, the solubility in water, the thermal and morphological characteristics and the digestibility of starches (Kim *et al.,* 2001; Huang *et al.,* 2008; Moraes *et al.,* 2013; Juarez-Arellano *et al.,* 2019; Yang *et al.,* 2021).

The properties of milled materials, as well as the particle size distribution, viscosity profile and the degree of disorder, depend on the grinding conditions, such as: grinding materials (for example, silicon nitride, ceramic, stainless steel and tungsten carbide), grinding speed, grinding time, grinding media (eg dry grinding or wet grinding), diameter of grinding balls, proportion of sample/balls and grinding temperature (El-Eskandarany, 2015). Therefore, there are many factors that should be limited to obtain feasible starch-based nanocarriers, and many experimental works could be necessary, so an alternative would be to use the methods of mathematical modeling to obtain the most favorable properties in starch by mechanical grinding modification: starch granule size <7 μm and viscosity≤0.01 Pa·s in water suspension.

However, the result of the application of simulation tools is heavily dependent on the quality of the mathematical model (Carrillo-Ahumada *et al.,* 2020; Nogales *et al.,* 2022; Buddhakulsomsiri *et al.,* 2018; Maraphum *et al.,* 2022; Melgarejo-Torres *et al.,* 2022; Gutierrez-Antonio *et al.,* 2022). Also, it has been observed that the process dynamics are nonlinear, which has made the modeling task even more complex (Feil *et al.,* 2004; Castillo-Santos *et al.,* 2017; Toro *et al.,* 2018). Modifying the processes results in a novel situation, and, a vast set of experiments needs to be performed in order to generate data which can be used to construct novel models to describe the new process. Therefore, the development of a phenomenological process model has become a difficult task (Santamaria *et al.,* 2021; Li *et al.,* 2022; Rovalino-Córdova *et al.,* 2021; Manepalli and Alavi 2021). In view of these difficulties, different methodologies have been used to model the behavior of starch. Among these methodologies are Genetic Programming (GP) is based on input-output data instead of conventional regression (Ramírez-Hernández *et al.,* 2017). Response Surface (RS) with polynomial models (Tijsen *et al.,* 1999; Barua *et al.,* 2021; Hamidi *et al.,* 2021; Matkowski and Lisowski 2020; Wang *et al.,* 2021; Pandey *et al.,* 2020; Oluwasina *et al.,* 2020; Das *et al.,* 2022; Setyaningsih *et al.,* 2021; Kizhakedathil *et al.,* 2021; Kristiawan *et al.,* 2019) use a large data-set to obtained a phenomenological model. The curve Fitting Toolbox$^{\text{TM}}$ of Matlab$^{®}$ MathWorks (2008) has been used to obtained different model structures (Wen *et al.,* (2012); Al-Malah *et al.,* (2009); Ghosh (2018); Hallauer *et al.,* (2007)). Curve Fitting Toolbox$^{\text{TM}}$ of Matlab$^{®}$ (MathWorks (2008)) provides an app and functions for fitting curves and surfaces to data with input and output date. The structures of mathematical models and tools that the app has available are: exponential, Fourier, Gaussian, interpolant, linear fitting, polynomial, power and rational. After choosing the structure of the mathematical model, the parameters are chosen by means of numerical optimization. In this work were used rational models because represents of better way the experimental data.

Specifically, the rational models are defined as ratios of polynomials:

$$y = \frac{\sum_{i=1}^{n+1} p_i x^{n+1-i}}{x^m + \sum_{i=1}^{m} q_i x^{m-1}} \tag{1}$$

where n is the degree of the numerator polynomial and $0 \leq n \leq 5$, while m is the degree of the denominator polynomial and $1 \leq m \leq 5$. The main advantage of rationals is their flexibility with data that has complicated structure. To evaluate the fit between the model and the experimental data, the following indexes are used: SSE, R^2 and $RMSE$.

The coefficients of determination SSE (Equation 2), R^2 (Equation 3) and $RMSE$ (Equation 4) describes the adjustment between the experimental data and the calculated data. The aim is to obtain a model that can explain the process conditions in the production of modified starches to be used as wall materials in the nano-encapsulation of compounds by nano-spray drying.

$$SSE = \sum_{k=1}^{N} ((y(k) - \hat{y}(k))^2 \tag{2}$$

$$R^2 = 1 - \frac{SSE}{\sum_{k=1}^{N} (\hat{y}(k))} \tag{3}$$

$$RMSE = \frac{\sqrt{SSE}}{N} \tag{4}$$

where N is the number of samples used for model identification, $y(k)$ is the experimental output, $\hat{y}(k)$ is the calculated output and k is the sample.

In decision making stage, data visualization tools are important to the designer/experimenter. In addition, it is established which conditions are feasible and infeasible for the entire data set obtained by mean the models. Specifically, what operating conditions are suitable for the experimenter in a graphic way.

The aim of this work was to evaluate the properties of viscosity and particle size distribution of starches modified by mechanical milling at different times and to model these study variables (using Curve Fitting Toolbox of Matlab$^{\text{TM}}$) to predict the operation conditions that allow to obtain a feasible starch-based nanocarrier than could be use in a nano-spray dryer B-90 from Büchi Company, which to carry out the dried process requires particle sizes $< 7\ \mu$m and viscosities ≤ 0.01 Pa·s in the feed mixtures.

The structure of the article is the following: Section 2 shows the experimental and computational methodologies; The results and discussion are shown in Section 3. Finally, some remarks are exposed in conclusions.

2 Methodology

2.1 *Material*

The tubers of chayotextle (*Sechium edule Sw*) were purchased from producers in Tulancingo, Hidalgo, Mexico.

2.2 *Methods*

2.2.1 *Starch isolation*

Chayotextle starch was isolated using the method proposed by Flores-Gorosquera *et al.,* (2004) with slight modifications. The tubers were cut into 2×2 cm cubes and immediately macerated at low speed in a blender (500 g of root per 500 g of water) for 2 min. The homogenate was sieved consecutively, using 50, 100, 200, 270 and 325 US mesh, and washed until the wash water was clear. The starch solution settled overnight and was then decanted. This material was dried in a convection oven at 35 ºC overnight. The dried starch was ground to a powder and then sieved through a standard 100 mesh. The starch powder was stored in a sealed container until use.

2.2.2 *Starch modification by high-energy mechanical milling*

To carry out high-energy mechanical milling, 8.0 g of sample was placed in an 80 mL siliconnitride bowl and 15 siliconnitride balls of 10 mm diameter were added to each bowl. Mechanical grinding was carried out using a mill (FRITSCH, Planetary Micro MillPulverisette 7; Idar-Oberstein, Germany) at times of 20, 30, 40, 50, 60, 70 and 80 min. The grindings were carriedout dry method, speed of 700 rpm, in cycles of 5 min of grinding and 10 min of cooling to avoid heating the bowls and therefore avoid any unexpected modification.

2.3 *Characterization of modified starch*

2.3.1 *Profile Pasting*

For the modified starch paste formation profile, a 10 % (w/v) dispersion was prepared, for which a rheometer (TA Instruments, Discovery HR-2 Hybrid; New Castle, DE, USA) equipped with a starch pasting cell (Smart Swap^{TM}, SPC 110533; New Castle, DE, USA) was used. The dispersion was subjected to a heating-cooking-cooling cycle according to Ramírez-Hernández *et al.,* (2020). The initial temperature was 30 ºC which was maintained for 60 s, then heating to 90 ºC was performed at a heating rate of 15 ºC min^{-1} and the temperature was maintained for 10 min (cooking) and finally cooled to 30 ºC at a speed of 30 ºC min^{-1}, keeping at this temperature for 7 min. Trios software version 4 (TA Instruments; New Castle, DE, USA) was used to obtain the parameters of paste temperature, peak viscosity, cool paste viscosity, and final viscosity from the grazing curve.

Particle size distribution is defined as the relative percentage of grains of each of the different size fractions represented in a sample (Perry *et al.,* 2001).

The particle size distribution of the flours was determined by laser diffraction using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK). Powders samples were dispersed using a Scirocco dry dispersion unit (Malvern, Worcestershire, UK) at a feed pressure of 2 bars and a feedrate of 40 %.

The obscuration was in the interval from 0.5 to 5%. The Fraunhofer approximation was used for the calculation of particle size. The volume, particle size distribution and average values were determined from at least three experimental runs.

2.3.2 Computational methodology

In this section shows the computational methodology of this research work. Firstly, the experimental data of the starches was observed. Subsequently, with the experimental data and the use of Curve Fitting Toolbox^{TM} of Matlab$^{®}$, a set of nonlinear mathematical models were identified that represents the variable responses: volume (%) in function of size (μm), and viscosity (Pa·s) in function of sample. Then, to validate the models obtained, correlation indices of the model *vs*. experimental data were performed. Finally, by mean of decision making stage were statement factible and non-factible and selected areas of conditions in function of a specific size both of them at different times.

3 Results and discussion

3.1 Characterization of modified starch

3.1.1 Profile Pasting

The native starch of Chayotextle presented high values of maximum viscosity of 8 Pa·s (Figure 1).

Chavarria-Fernandez *et al.,* (2021) reported similar values for chayotextle flour. These results indicate that this source of starch has very high viscosities at gelatinization temperatures, being a very important limitation to consider to be used as a wall material in the nano-encapsulation of bioactive compounds using nano-spray draying equipment, since this equipment requires a very low viscosity (0.01 Pa.s). However, the modification by high-energy mechanical grinding decreased the maximum viscosity significantly with increasing grinding time up to 40 min. This is due to the fact that the energy generated by grinding caused a breakdown of the crystalline zones of amylopectin, causing a decrease in viscosity. It has been reported that the maximum viscosity is influenced by the structure of amylopectin (Juarez-Arellano *et al.,* (2019)). Juarez-Arellano *et al.,* (2021) reported a similar behavior for potato starch, where they observed that mechanical milling significantly decreased maximum viscosity, swelling power and crystallinity by increasing the energy supply by mechanical milling. An opposite behavior was observed in the cooling stage, since the viscosity during this stage increased significantly compared to the maximum viscosity (Heating stage). This is due to the fact that mechanical grinding generates a mechano-hydrolysis of the starch polymers causing an increase in amylose content (Moraes *et al.,* 2013) and as a consequence an increase in retrogradation of the starch during the cooling stage.

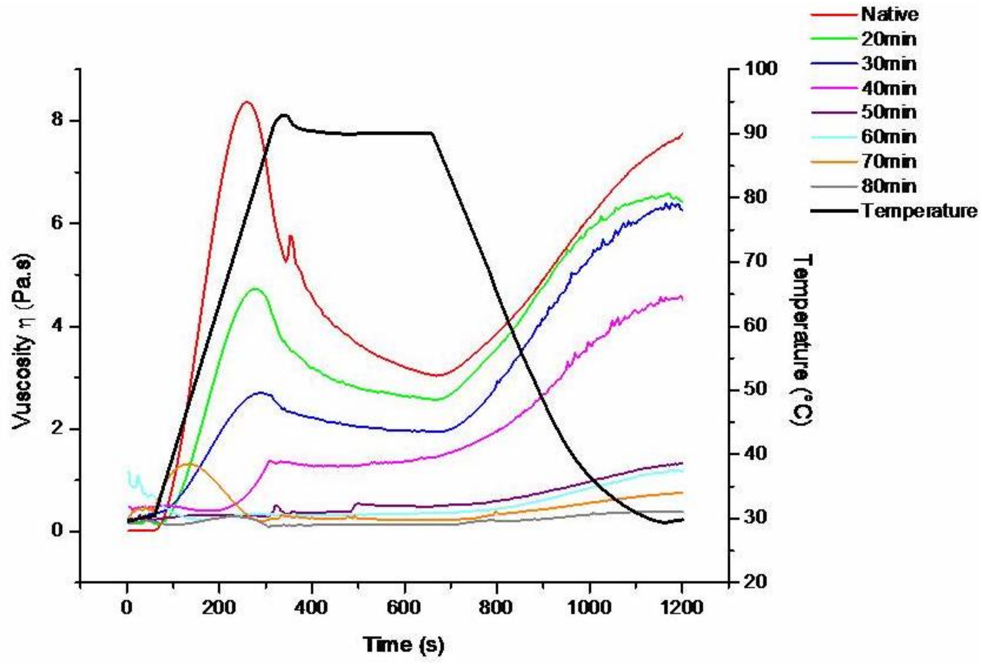

Fig. 1. Pasting profile of starches modified by mechanical milling at different times.

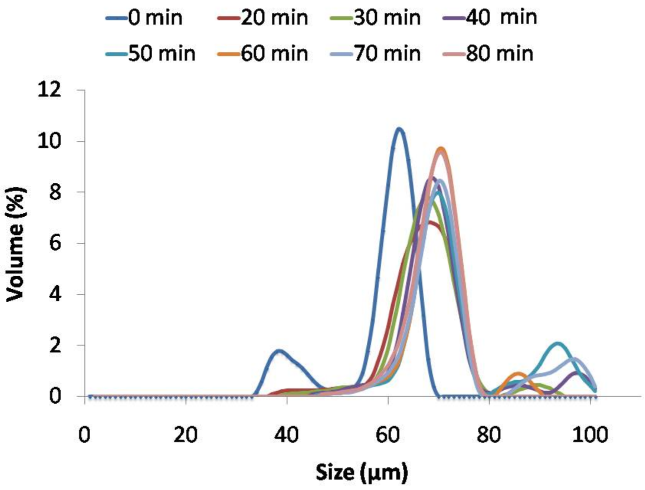

Fig. 2. Particle size distribution of starches modified by mechanical milling at different times.

Mechanical grinding affects the structure of amylopectin, mainly the amorphous zones (the branch points or α-1,6 bonds) which are more susceptible to breakage due to the energy supplied by the impact of the balls with starch, releasing short linear chains (amylose) (Cavalliniand Franco, 2010) that during cooling are capable of trapping water molecules increasing viscosity. Such short fractions can have a positive impact on the encapsulation of bioactive compounds. Several authors have reported an improvement in the encapsulation efficiency of beta carotenes instarches modified by mechanical milling (Morrison *et al.,* 1993; Roa *et al.,* 2017; Gonzalez *et al.,* 2020). However, there are few studies focused on the nanoecapsulation of bioactive compounds using nano spray drying equipment, so mechanical grinding is a viable alternative to obtain wall materials with desirable rheological characteristics.

On the other hand, at high milling times (50 to 80 min) it was no longer possible to determine the viscosity profile of the starch, this indicates that the granular structure of the starch was completely lost, obtaining an amorphous polysaccharide.

3.1.2 Particle size distribution (PSD)

Chayotextle starch showed a multimodal particle size distribution with 3 populations of sizes 38, 63 and 92 μm, with 63 μm having the largest volume (Figure 2).

These sizes of starch granules do not favor their use in the nano-encapsulation of compounds through the nano-spray draying technique, since the equipment requires sizes from 7 μm to nm, so it is necessary to reduce the particle size. On the other hand, mechanical grinding showed a mono modal distribution at all grinding times; however, the size of the particles increased with mechanical grinding time. This behavior is due to the formation of agglomerates during mechanical grinding, Since the decrease in particle size increases the surface area, promoting the agglomeration of starch granules by Van der Waals forces (Li *et al.,* 2014; Soe *et al.,* 2020; Huang *et al.,* 2021; Zhang *et al.,* 2021).

Several authors have reported behavior like this study. Jhan *et al.,* (2021) reported that ball milling caused starch granule fragmentation. Gonzalez *et al.,* (2018) reported that the native starches showed a bimodal distribution and during the milling process, said granule size distribution changed to monomodal.

3.2 Model identification of the modified starches as wall materials in the nano-encapsulation

Experimental results of viscosity and size distribution of particle are not the ideal ones to use those modified starches as wall material in the nano-encapsulation of bioactive compounds using the nano-spray drying equipment.

For this reason, a modeling of the operating variables was carried out of mechanical grinding to elucidate the best operating conditions and obtain modified starches with required viscosities and particle sizes two to be used as wall material in nano-encapsulation.

The models of modified starches as wall materials in the nano-encapsulation are the following:

$$Volume = \frac{(p_{11}Sz^5 + p_{12}Sz^4 + p_{13}Sz^3 + p_{14}Sz^2 + p_{15}Sz + p_{16})}{(q_{10}Sz^5 + q_{11}Sz^4 + q_{12}Sz^3 + q_{13}Sz^2 + q_{14}Sz + q_{15})} \tag{5}$$

$$Viscosity = \frac{(p_{21}Sp^5 + p_{22}Sp^4 + p_{23}Sp^3 + p_{24}Sp^2 + p_{25}Sp + p_{26})}{(q_{20}Sp^5 + q_{21}Sp^4 + q_{22}Sp^3 + q_{23}Sp^2 + q_{24}Sp + q_{25})} \tag{6}$$

where Equation (5) is a correlation between volumen [=]% and Sz (size, μm), Equation (6) is a correlation between viscosity [=]Pa·s and Sp (sample). Considering different times: 0, 20, 30, 40, 50, 60, 70 and 80 min. The parameters $p_{i,j}$ with $i = 1,2$ and $j = 1,2,...,6$ and $q_{i,k}$ with $k = 0,1,2,...,6$ are described in Table 1 and 2.

Numerical simulation of Equations (5) and (6) with the parameters described in the Table 1 and 2 with its respectively times are shown in Figures 3 and 4.

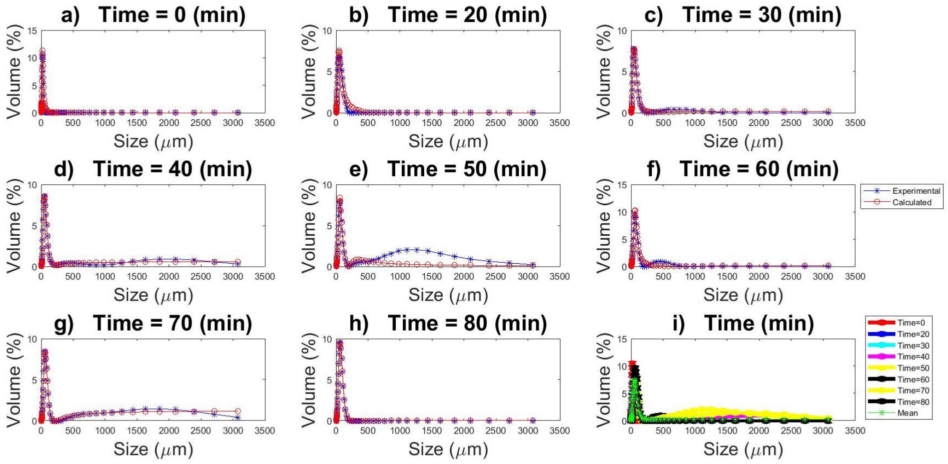

Fig. 3. Validation of the mathematical model (Equation 5) *vs*. experimental data: a) $Time$ = 0 min, b) $Time$ = 20 min, c) $Time$ = 30 min, d) $Time$ = 40 min, e) $Time$ = 50 min, f) $Time$ = 60 min, g) $Time$ = 70 min, h) $Time$ = 80 min. i) Mean of all times.

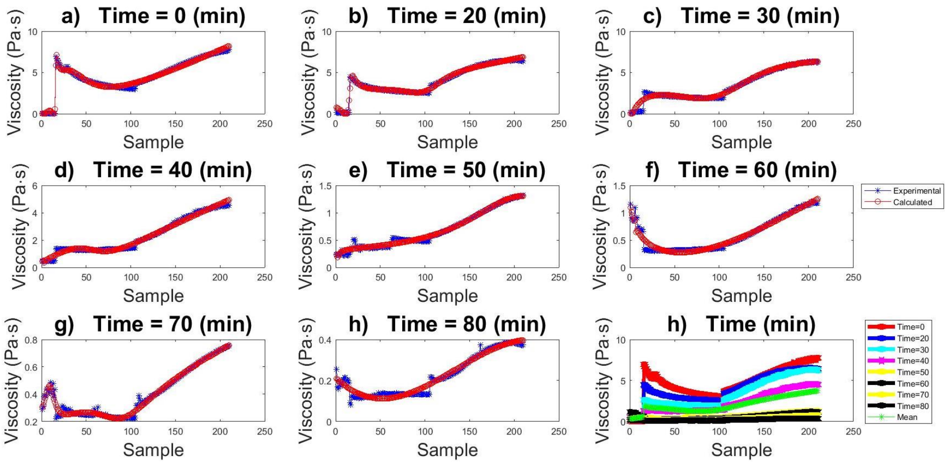

Fig. 4. Validation of the mathematical model (Equation 6) *vs*. experimental data: a) $Time$ = 0 min, b) $Time$ = 20 min, c) $Time$ = 30 min, d) $Time$ = 40 min, e) $Time$ = 50 min, f) $Time$ = 60 min, g) $Time$ = 70 min, h) $Time$ = 80 min. i) Mean of all times.

Table 1. $p_{11,12,...16}$ and $q_{10,11,...16}$ parameters with different temperatures of Equation (5).

Time (min)	Parameters
0	$p_{11} = -0.3459$, $p_{12} = 59.4$, $p_{13} = -341.9$, $p_{14} = 739.4$, $p_{15} = -375.1$, $p_{16} = 38.39$ $q_{10} = 1.0$, $q_{11} = 590$, $q_{12} = -1487$, $q_{13} = 1456$, $q_{14} = -438$, $q_{15} = 0$
20	$p_{11} = -0.4472$, $p_{12} = 237.6$, $p_{13} = -762.6$, $p_{14} = 847.8$, $p_{15} = -386.5$, $p_{16} = 60.02$ $q_{10} = 1.0$ $q_{11} = -67.87$ $q_{12} = 2357$, $q_{13} = -5585$, $q_{14} = 4078$, $q_{15} = -867.5$
30	$p_{11} = 0.2091$, $p_{12} = -98.08$, $p_{13} = 1.616 \times 10^4$, $p_{14} = 3.797 \times 10^4$, $p_{15} = 1.971 \times 10^5$, $p_{16} = -1.488 \times 10^5$ $q_{10} = 1.0$, $q_{11} = -189.5$, $q_{12} = 1.601 \times 10^4$, $q_{13} = -5.227 \times 10^5$, $q_{14} = 7.818 \times 10^6$, $q_{15} = -5.271 \times 10^6$
40	$p_{11} = 0.6124$, $p_{12} = -241.2$, $p_{13} = 2.764 \times 10^4$, $p_{14} = -1.533 \times 10^5$, $p_{15} = 1.533 \times 10^6$, $p_{16} = -1.247 \times 10^5$ $q_{10} = 1.0$, $q_{11} = -207.5$, $q_{12} = 1.904 \times 10^4$, $q_{13} = -7.114 \times 10^5$, $q_{14} = 1.181 \times 10^7$, $q_{15} = 5.671 \times 10^6$
50	$p_{11} = 0$, $p_{12} = 270.2$, $p_{13} = -1.069 \times 10^5$, $p_{14} = 1.07 \times 10^7$, $p_{15} = -2.292 \times 10^7$, $p_{16} = 8.063 \times 10^5$ $q_{10} = 1.0$, $q_{11} = -510.2$, $q_{12} = 9.52 \times 10^4$, $q_{13} = -6.624 \times 10^6$, $q_{14} = 1.871 \times 10^8$, $q_{15} = -6.804 \times 10^6$
60	$p_{11} = 0.2335$, $p_{12} = -205$, $p_{13} = 7.423 \times 10^4$, $p_{14} = -2.107 \times 10^5$, $p_{15} = 1.479 \times 10^5$, $p_{16} = -2.764 \times 10^4$ $q_{10} = 1$ $q_{11} = 161.6$, $q_{12} = -2.778 \times 10^4$, $q_{13} = 1.237 \times 10^6$, $q_{14} = -1.259 \times 10^6$, $q_{15} = 2.809 \times 10^5$
70	$p_{11} = 1.244$, $p_{12} = -550.4$, $p_{13} = 5.664 \times 10^4$, $p_{14} = 3.669 \times 10^5$, $p_{15} = -5.199 \times 10^4$, $p_{16} = 400.8$ $q_{10} = 1.0$ $q_{11} = -242.7$, $q_{12} = 2.892 \times 10^4$, $q_{13} = -1.453 \times 10^6$, $q_{14} = 3.707 \times 10^7$, $q_{15} = -3.771 \times 10^5$
80	$p_{11} = 0.06458$, $p_{12} = -63.63$, $p_{13} = 7443$, $p_{14} = 7.739 \times 10^5$, $p_{15} = -8.089 \times 10^5$, $p_{16} = 9074$ $q_{10} = 1.0$ $q_{11} = -249.7$, $q_{12} = 2.59 \times 10^4$, $q_{13} = -1.174 \times 10^6$, $q_{14} = 2.44 \times 10^7$, $q_{15} = 4.82 \times 10^5$

Table 2. $p_{11,12,...16}$ and $q_{10,11,...16}$ parameters with different temperatures of Equation (6).

Time (min)	Parameters
0	$p_{21} = 0.05021$, $p_{22} = -6.797$, $p_{23} = 434.3$, $p_{24} = -9599$, $p_{25} = 7.973 \times 10^4$, $p_{26} = -1.95 \times 10^5$ $q_{20} = 0.0$, $q_{21} = 1.0$, $q_{22} = -81$, $q_{23} = 3293$, $q_{24} = -5.876 \times 10^4$, $q_{25} = 3.65 \times 10^5$
20	$p_{21} = 0.02165$, $p_{22} = -3.013$, $p_{23} = -73.69$, $p_{24} = 2.15 \times 10^4$, $p_{25} = -4.373 \times 10^5$, $p_{26} = 2.264 \times 10^6$ $q_{20} = 0$ $q_{21} = 1.0$ $q_{22} = -237.5$, $q_{23} = 1.805 \times 10^4$, $q_{24} = -4.03 \times 10^5$, $q_{25} = 2.83 \times 10^6$
30	$p_{21} = 6.499$, $p_{22} = -1185$, $p_{23} = 6.497 \times 10^4$, $p_{24} = -1.932 \times 10^5$, $p_{25} = -3555$, $p_{26} = 5.293 \times 10^4$ $q_{20} = 1.0$, $q_{21} = -194.8$, $q_{22} = 1.202 \times 10^4$, $q_{23} = 1.726 \times 10^5$, $q_{24} = 4.957 \times 10^4$, $q_{25} = 1.109 \times 10^4$
40	$p_{21} = 0.02719$, $p_{22} = -3.642$, $p_{23} = 143.2$, $p_{24} = 593.5$, $p_{25} = -1.723 \times 10^4$, $p_{26} = 4.12 \times 10^4$ $q_{20} = 0$, $q_{21} = 1.0$, $q_{22} = -118.4$, $q_{23} = 5651$, $q_{24} = -5.035 \times 10^4$, $q_{25} = 9.892 \times 10^4$
50	$p_{21} = 0.2745$, $p_{22} = -97.29$, $p_{23} = 1.648 \times 10^4$, $p_{24} = -1.75 \times 10^4$, $p_{25} = 3824$, $p_{26} = 1.061 \times 10^4$ $q_{20} = 1.0$, $q_{21} = -407.6$, $q_{22} = 4.762 \times 10^4$, $q_{23} = 1.017 \times 10^6$, $q_{24} = 1498$, $q_{25} = -1155$
60	$p_{21} = -1.409 \times 10^{-7}$, $p_{22} = 7.701 \times 10^{-5}$, $p_{23} = -0.00508$, $p_{24} = 0.1955$, $p_{25} = 10.1$, $p_{26} = -74.22$ $q_{20} = 0$ $q_{21} = 0$, $q_{22} = 0$, $q_{23} = 1.0$, $q_{24} = 2.872$, $q_{25} = -62.13$
70	$p_{21} = 0.003161$, $p_{22} = -0.4339$, $p_{23} = 2.879$, $p_{24} = 1597$, $p_{25} = -3.537 \times 10^4$, $p_{26} = 3.37 \times 10^5$ $q_{20} = 0$ $q_{21} = 1.0$, $q_{22} = -186$, $q_{23} = 1.187 \times 10^4$, $q_{24} = -1.871 \times 10^5$, $q_{25} = 1.17 \times 10^6$
80	$p_{21} = 0$, $p_{22} = -1.258 \times 10^7$, $p_{23} = 5.144 \times 10^5$, $p_{24} = -0.004496$, $p_{25} = -0.2335$, $p_{26} = -0.9315$ $q_{20} = 0$ $q_{21} = 0$, $q_{22} = 0$, $q_{23} = 0$, $q_{24} = 1.0$, $q_{25} = -4.336$

Table 3. Fit indices of Equation 5 at different times.

Time (min)	R^2	$RMSE$	SSE
0	0.9761	0.3661	13.40
20	0.9708	0.3458	11.95
30	0.9970	0.1132	1.2815
40	0.9971	0.1130	1.2768
50	0.9402	0.4661	21.7267
60	0.9824	0.3082	9.5010
70	0.9969	0.1121	1.2563
80	0.9998	0.0356	0.1266

Table 4. Fit indices of Equation 6 at different times.

Time (min)	R^2	$RMSE$	SSE
0	0.9845	0.2383	11.93
20	0.9846	0.2199	10.15
30	0.9773	0.2706	15.37
40	0.9861	0.1517	4.83
50	0.9860	0.0389	0.3175
60	0.9673	0.0549	0.6331
70	0.9834	0.0221	0.1022
80	0.9627	0.0191	0.0766

Figure 3 shows that for the times from 0 to 80 min (3a, 3b,...,3h) the model (Equation 5) adequately represents the experimental data of the volume (%). Figure 3i shows the value of the response of the model and the means of the set of times obtained. Figure 4 shows that for the times from 0 to 80 min (4a, 4b,...,4h) the model (Equation 6) adequately represents the experimental data of the viscosity (Pa·s). Figure 4i shows the value of the response of the model and the means of the set of times obtained.

Validation of the model with the experiments data are evaluated with fit indices are shown in Table 3 and 4 with $R^2 > 0.96$ $RMSE < 0.23$ and $SSE < 21.7$ for both equations.

Up to this point a model that fits the experimental data, but a decision stage to obtain the operating conditions required by the experimenter.

3.3 Decision Making stage with the model

In this research work are presented the factible (what the experimenter requires), non-factible (what the experimenter does not require) and selected (what the experimenter requires more specifically) areas of process conditions.

The selection criterion is that of all samples are considered factible with size 1 to 7 μm and viscosity≤0.01 Pa·s are shown in Figures 5a-5c and 6a-6c.

The model allowed elucidating the operating conditions for mechanical milling from experimental data raised by the experimenter that allows obtaining modified starches in short times. This mathematical modeling is an alternative for obtaining modified starches with specific properties of viscosity and particle size to be used in nano-encapsulation.

Other starch modification methods such as acid hydrolysis nine days, (Aparicio-Saguilán *et al.,* 2014) seven days (Aparicio-Saguilán *et al.,* 2015) have been reported to produce changes in starch properties. However, this method requires very long hydrolysis times compared to this proposed methodology.

Conclusion

The models obtained for the modification of starch indicate that under evaluated conditions both 20 and 30 min of mechanical grinding allow to obtain wall materials with viscosities and particle sizes that favor their use in nano-spray drying equipment. The model obtained for this type of starch represents the volume (%) and the viscosity (Pa·s) with its respective operating conditions, it had a fit with the experimental data of $R^2 > 0.96$, $RMSE < 0.23$ and $SSE < 220$. With this model, it is possible to determine the feasible operating conditions for this process.

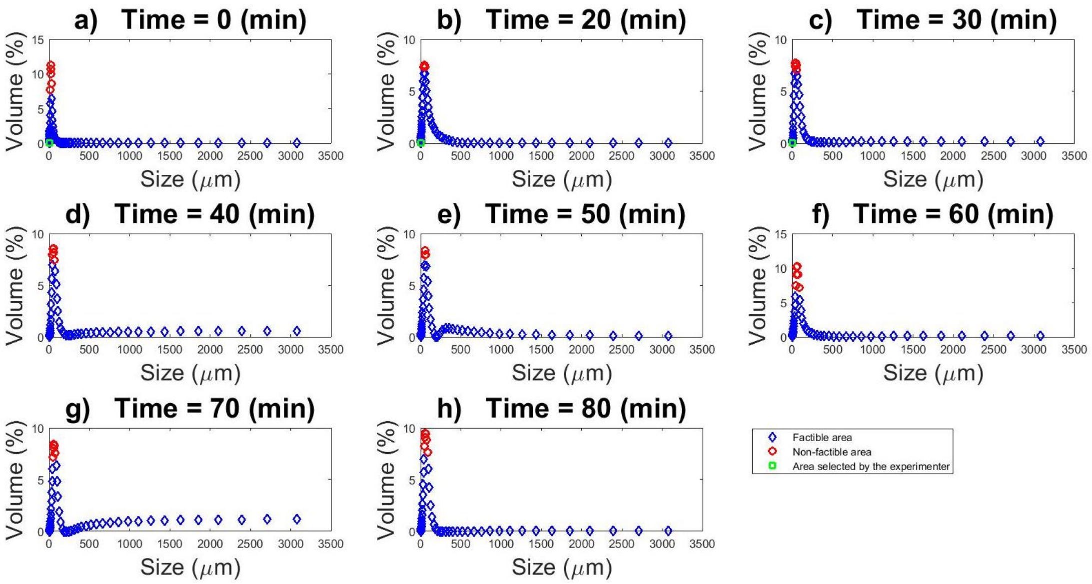

Fig. 5. Factible, non-factible and selected areas of the mathematical model (Equation 5): a) $Time = 0$ min, b) $Time = 20$ min, c) $Time = 30$ min, d) $Time = 40$ min, e) $Time = 50$ min, f) $Time = 60$ min, g) $Time = 70$ min, h) $Time = 80$ min.

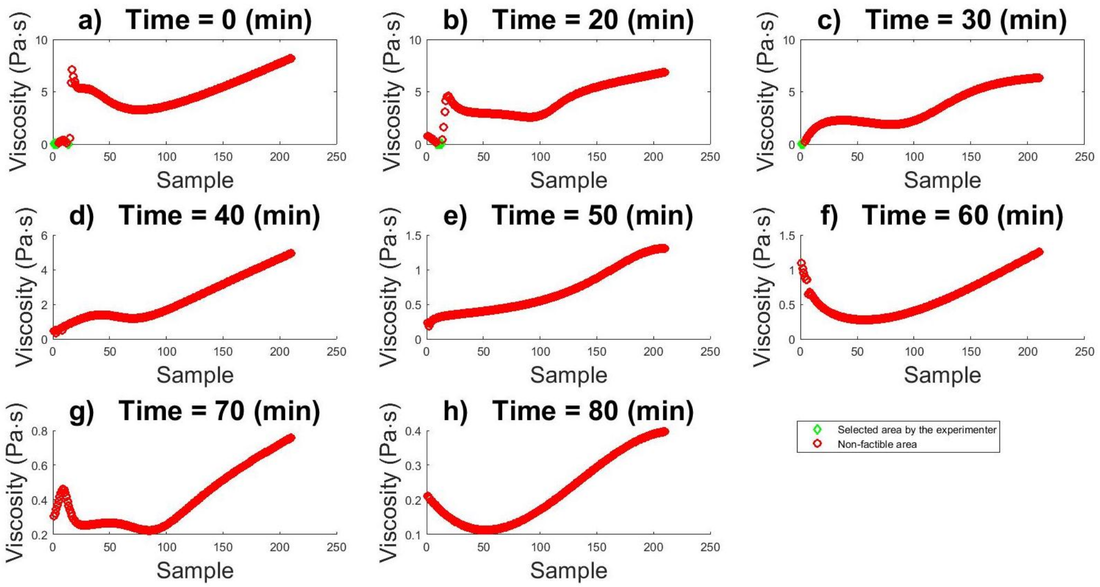

Fig. 6. Selected and non-factible areas of the mathematical model (Equation 6): a) $Time$ = 0 min, b) $Time$ = 20 min, c) $Time$ = 30 min, d) $Time$ = 40 min, e) $Time$ = 50 min, f) $Time$ = 60 min, g) $Time$ = 70 min, h) $Time$ = 80 min.

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