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Proceeding Paper

Determination of Critical Storage Conditions for Spray-Dried Habanero Pepper (*Capsicum chinense*) Extracts by Coupling Water Adsorption Isotherms and Glass Transition Temperature †

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† Presented at the 4th International Electronic Conference on Foods, 15–30 October 2023; Available online: https://foods2023.sciforum.net/.

Abstract: This study aimed to determine storage conditions for microparticles containing habanero pepper extracts with maltodextrin (MD) and a 95:5 *w*/*w* mixture with precipitated silica (MDSP) as wall materials. State diagrams (SD) using water adsorption isotherms and glass transition temperatures were created. Monolayer values were 6.17 g (MD) and 6.76 g (MDSP) of water/100 g d.s. Critical water activity values (a_wC) were 0.49 for MD and 0.41 for MDSP. When stored at $a_w > a_wC$, both samples underwent physical transformations, with significant color changes ($\Delta E > 8$). Conversely, storage below a_wC resulted in minimal changes ($\Delta E < 4$), consistent with the SD.

Keywords: microencapsulation; physical stability; critical water activity

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Citation: Marín Castro, U.R.; Cansino Jácome, F.; Olguín-Rojas, J.A.; Rodríguez-Jimenes, G.d.C.; González Arnao, M.T.; Flores Andrade, E.; Rascón Díaz, M.P. Determination of Critical Storage Conditions for Spray-Dried Habanero Pepper (*Capsicum chinense*) Extracts by Coupling Water Adsorption Isotherms and Glass Transition Temperature. *Biol. Life Sci. Forum* **2023**, *26*, 97. https://doi.org/10.3390/Foods2023-151

Academic Editor: Manuel Viuda-Martos

Published: 17 October 2023

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1. Introduction

The ethanolic extract of habanero peppers contains two main groups of bioactive compounds—carotenoids and capsaicinoids—which are responsible for the characteristic color and pungency, respectively [1,2]. However, carotenoids are highly sensitive to heat, light, and oxidation due to their polymeric structure. To preserve and recover these bioactive compounds effectively, encapsulation processes offer a promising solution. Microencapsulation involves creating easily manageable particles with a protective polymeric coating, effectively shielding bioactive compounds from environmental factors [3]. This encapsulation technique enables the precise dosing of the active agent and has widespread applications in various industries. In pharmaceuticals, it is used for controlled drug release, while in the food industry, it is employed to manage sensory attributes like taste, color, aroma, and texture. Moreover, it allows for the incorporation of health-beneficial compounds [4,5]. Powders formed through spray drying should be able to be stored for extended periods without compromising their stability. However, structural changes in microparticles, such as stickiness, agglomeration, and caking, can occur when stored under conditions exceeding their critical storage parameters [6,7]. Understanding the water adsorption characteristics is crucial for predicting shelf life and determining the critical moisture content and water activity required for product acceptability, especially for products prone to deterioration due to increased humidity. Additionally, they play a significant role in drying, packaging, and storage processes [8]. A commonly used methodology to assess the stability of dehydrated foods is moisture adsorption isotherms, providing valuable information about the sorption phenomenon and aiding in stability predictions [7]. Recently, the concept of water activity has been linked to the glass transition. The glass transition temperature (T_g) serves as a reference parameter for characterizing the properties, quality, and stability of food systems, offering an integrated perspective on the role of water in foods [9]. Therefore, the objective of this research was to determine the optimal storage conditions for microparticles containing habanero pepper ethanolic extracts, using two different wall materials: maltodextrin and a mixture with precipitated silica (95:5 w/w). The study also aimed to assess the impact of storage conditions on the surface color of the microparticles.

2. Materials and Methods

2.1. Microparticles of Habanero Pepper Ethanolic Extract

Microparticles from red habanero pepper ethanolic extract were obtained using a spray dryer equipped with a heat pump and a dehumidifier (Büchi, Mod. B-290, Flawil, Switzerland). The system operated at an inlet temperature of 140 °C and an outlet temperature of 60 °C, with nitrogen utilized as the drying gas. The ethanolic extract was derived from red habanero peppers through maceration at 50 °C (20 g of chili pepper with 100 g of 70% w/w ethanol as the solvent). This extract was directly mixed with maltodextrin DE10 (MD) at a 4:1 ratio. Additionally, a mixture of the extract with precipitated silica (95:5) (MDSP) was used as supporting materials. The resulting microparticles were stored under vacuum in laminated bags at −20 °C for subsequent evaluations.

2.2. Water Vapor Adsorption Isotherms

The microparticles of the habanero extracts with MD and MDSP were placed in vacuum desiccators containing 20 g of phosphorous pentoxide (P_2O_5) for 20 days at room temperature. Moisture adsorption was determined by equilibrium moisture content at several water activity levels, which was determined by the static gravimetric method at 35 °C. Eight saturated salt solutions were prepared (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, and KCl) [10]. For data analysis, three models were applied to assess water adsorption: GAB, OSWIN, and LEWICKI (Equations (1)–(3), respectively) [11–13].

$$M = \frac{M_0 C_{GAB} K_{GAB} a_w}{(1 - K_{GAB} a_w)(1 - K_{GAB} a_w + C_{GAB} K_{GAB} a_w)} \tag{1}$$

$$M = A \left[\frac{a_w}{1 - a_w} \right]^B \tag{2}$$

$$M = A \left(\frac{1}{a_w} - 1 \right)^{B-1} \tag{3}$$

where a_w is the water activity; M is the moisture content of the sample on a dry basis (g of water/100 g dry weight); M_0 is the monolayer moisture content (g of water/100 g dry weight); C_{GAB} and K_{GAB} are constants related to the temperature effect; and A and B are constants specific to the model. Isotherm modeling and graph construction were carried out using Kaleida Graph 4.0 software. The goodness of fit of the data was assessed using the relative mean deviation modules, $E\%$, according to Equation (4) [14].

$$E\% = \frac{100}{n} \sum_{i=1}^{n} \frac{|Mi - Mpi|}{Mi} \tag{4}$$

where Mi is the experimental moisture content; Mpi is the model-predicted moisture content; and n is the number of observations.

2.3. Calorimetric Analysis

T_g was determined using a Differential Scanning Calorimeter (MDSC Q2000, TA INSTRUMENTS, New Castle, DE, U.S.A.). Samples (5 mg) stored in a_w = 0.3 were transferred to aluminum pans and hermetically sealed. Initially, the samples were cooled to −40 °C; then, an isothermal process was performed for 10 min, and finally, samples were heated at 5 °C/min until a temperature of 120 °C was reached, using the amplitude of 1.272 °C and a period of 60 s. T_g was determined as the onset point of the step change on the heat flow curve. The experimentally obtained T_g data were modeled using the Gordon–Taylor equation and water adsorption data. The plasticizing effect of water on the transition was described by the Gordon–Taylor model [15], where the temperature was taken as −138 °C (Equation (5)).

$$T_g = \frac{x_1 T_{g1} + K x_2 T_{g2}}{x_1 + K x_2} \quad (5)$$

where T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the binary mixture, dry microcapsule, and water (−137 °C), respectively; x_1 and x_2 are the molar fraction or weight fraction of the dry microcapsule and water, respectively; and K is the arithmetic average of a series of K values that are obtained by solving the equation for a series of binary systems at different ratios of dry food and water.

2.4. Changes in Surface Color

The color determination was carried out by employing a Hunter-Lab colorimeter (Hunter Lab, Reston, VA, USA); the color of a sample is denoted by three dimensions, L^*, a^*, and b^*. Total color change (ΔE) was determined with Equation (6), where a lower ΔE value represents better color retention [16].

$$\Delta E = \sqrt{\left(L^* - L_0^*\right)^2 + \left(a^* - a_0^*\right)^2 + \left(b^* - b_0^*\right)^2} \quad (6)$$

where L^* represents the brightness of the color, a^* is the range in red (+) and green (−), and b^* is the range in yellow (+) and blue (−) after 4 weeks of storage. L_0^*, a_0^*, and b_0^* are the values of microcapsules at time zero.

3. Results and Discussions

Adsorption Isotherms and Critical Storage Conditions

Table 1 shows the parameters of experimental data fitted, with different models, to water sorption isotherms of microparticles of habanero extracts with MD and MDSP as wall materials. The GAB model showed the best fit (E%: 4.57%) for MD and MDSP; a model was considered acceptable when the value of E% was less than 10% and R^2 was greater than 0.9 [17]. The constant monolayer (M_0) predicted by GAB is an important stability parameter, because at this point, a product should be stable against microbial spoilage [9]. The isotherm exhibited Type II behavior, as per the Brunauer–Emmet–Teller classification [18].

The glass transition temperature of the capsules is dependent on both the moisture content and water activity within the food matrix, serving as predictive indicators for stability during storage. The combined influence of temperature and water content serves as a plasticizing agent within food matrices [6]. The critical water activity (a_wC) values signify the point at which a product's glass transition temperature matches room temperature. When the temperature exceeds this threshold, amorphous powders become vulnerable to detrimental transformations, such as collapse, stickiness, and caking, leading to a degradation in product quality [6,19]. The critical water activity value was determined to be 0.49 for MD (Figure 1).

Similar results were previously reported for paprika powder produced via spray drying with maltodextrin as the encapsulating material, yielding an a_wC of 0.496 [20], as well as for acai microparticles, with an a_wC of 0.574 [19]. In contrast, the incorporation of precipitated silica (5% w/w) led to a reduction in the glass transition temperature and an augmentation in the monolayer adsorption capacity on the particle surface. Consequently, the critical water activity values decreased from 0.49 to 0.41 for MDSP, indicating the reduced stability of the microparticles. This reduction in stability increased the likelihood of the microparticles transitioning into a rubbery state, causing physical transformations in the samples, ultimately resulting in collapse and caking.

Table 1. Estimated parameters from GAB, OSWIN, and LEWICKI models for microparticles of habanero extracts with MD and MDSP as wall materials.

Model	Parameter	MD	MDSP
GAB	M_0 (g of H_2O/100 g) d.s.)	6.17	6.79
	C_{GAB}	12.21	14.64
	K_{GAB}	0.97	0.96
	R^2	0.99	0.99
	$E\%$	4.57	3.17
LEWICKI	A	11.07	12.28
	B	0.34	0.36
	R^2	0.99	0.99
	$E\%$	21.74	7.75
OSWIN	A	11.07	12.28
	B	0.65	0.63
	R^2	0.99	0.99
	$E\%$	7.86	21.24

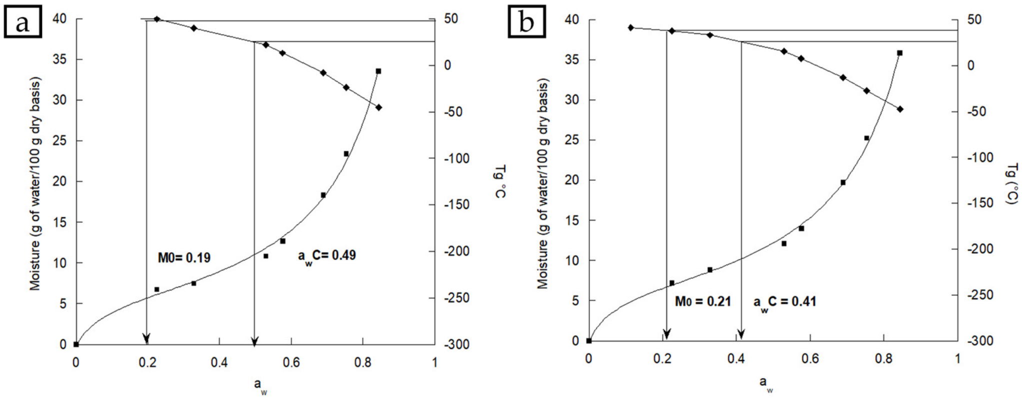

Figure 1. Variation in glass transition temperature and moisture content with water activity for microparticles of habanero extract with MD (**a**) and MDSP (**b**) as wall material.

In Figure 2, the total color variation observed during storage at different water activity values is present. The addition of precipitated silica within the evaluated range (5%, *w*/*w*) had no significant effect on color preservation. Minimal color variation (ΔE: 1.0 to 5.0) was observed at a_w levels ranging from 0.11 to 0.43. According to Obon et al. [21], when ΔE < 5.0, the human eye can only perceive minimal differences. The most significant variation in color retention occurs when particles are stored under conditions exceeding the a_wC [20]. ΔE increased with the increasing storage a_w of microparticles containing habanero pepper extract. This behavior is consistent with that reported for paprika powder [22], pumpkin [23], and borojó powder [24]. As mentioned earlier, at a_w values greater than a_wC, the capsules tend to collapse and cake, leading to the dilution of reactants within the capsule and, consequently, an increase in color change.

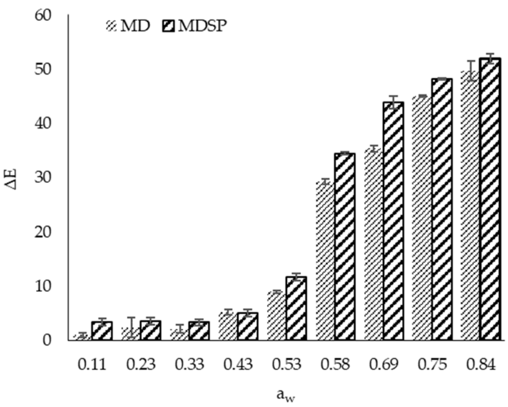

Figure 2. Variation in Δ*E* for microparticles of habanero extract with MD and MDSP as wall materials stored with different a_w values.

4. Conclusions

The GAB, OSWIN, and LEWICKI models accurately describe the adsorption of water onto microparticles containing habanero extracts with MD and MDSP as the wall material. Optimal color retention was achieved when the particles were stored below the critical water activity level (0.49 for MD and 0.41 for MDSP). These data enabled the determination of the critical water activity level for both materials, which was found to be 0.49 for MD and 0.41 for MDSP. Maintaining particles below the critical water activity level ensured optimal color retention. Although the moisture content corresponding to the monolayer (6.17 and 6.79 g of H_2O/100 g d.s., for MD and MDSP, respectively) is suggested as a point of maximum stability, to complete the present study, it is essential to evaluate the occurrence of chemical reactions, such as the degradation of capsaicinoids, during storage.

Author Contributions: Conceptualization, U.R.M.C. and J.A.O.-R.; methodology, U.R.M.C., M.P.R.D., M.T.G.A., J.A.O.-R. and F.C.J.; software, U.R.M.C., M.T.G.A. and E.F.A.; validation, U.R.M.C., M.P.R.D., J.A.O.-R., F.C.J. and G.d.C.R.-J.; formal analysis, U.R.M.C., J.A.O.-R. and E.F.A.; investigation, U.R.M.C., J.A.O.-R. and F.C.J.; resources, U.R.M.C., J.A.O.-R. and F.C.J.; data curation, U.R.M.C., J.A.O.-R. and M.T.G.A.; writing—original draft preparation, U.R.M.C. and J.A.O.-R.; writing—review and editing, U.R.M.C. and J.A.O.-R.; visualization, U.R.M.C., M.P.R.D., J.A.O.-R. and G.d.C.R.-J.; supervision, G.d.C.R.-J. and M.P.R.D.; project administration, G.d.C.R.-J.; funding acquisition, G.d.C.R.-J. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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