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Kinetics of water sorption and sugar crystallization in freeze-dried bananas previously immersed in concentrated sucrose and trehalose solution

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Resumen

Se deshidrataron osmóticamente rodajas de banana, utilizando soluciones de 45% p/p de sacarosa o trehalosa. Luego fueron liofilizadas a una actividad de agua (a_w) de aproximadamente 0,10. Los productos liofilizados se almacenaron a diferentes humedades relativas (%HR) durante 100 días para detectar la pérdida de humedad asociada a la cristalización del azúcar. Después de una absorción inicial de agua, no se observó pérdida de contenido de humedad absorbida en función de %HR, probablemente debido a la cristalización del azúcar. Estos cambios se explican utilizando valores de temperatura de transición vítrea (T_g) de literatura de los sistemas relacionados (banana liofilizada, sacarosa y trehalosa amorfas) en varias HR. El uso de trehalosa en lugar de sacarosa en el baño osmótico, dio lugar a una importante ventaja tecnológica puesto que la cristalización de las muestras se llevó a cabo a una mayor HR que la banana liofilizada sin tratamiento osmótico o aquella osmóticamente tratada con sacarosa.

Abstract

Banana slices were osmotically dehydrated in 45% w/w sucrose or trehalose solutions and freeze-dried to a water activity (a_w) of about 0.10. Freeze-dried products were stored at different relative humidities (%RH) up to 100 days to detect moisture loss associated with sugar crystallization. Following an initial water uptake, loss of sorbed moisture content was observed depending on %RH and this was likely due to sugar crystallization. These changes were adequately explained using literature glass transition temperature (T_g) values of related systems (freeze-dried banana, amorphous sucrose and trehalose) at various RH. The use of trehalose instead of sucrose in the osmotic bath, resulted in an important technological advantage since crystallization of the freeze-dried samples took place at higher RH than either for plain banana or that osmotically treated with sucrose.

Palabras clave

Liofilización, sacarosa, trehalosa, osmosis, cristalización, temperatura de transición *vítrea*.

Keywords
Freeze-drying; sucrose; trehalose; osmosis; crystallization; glass transition temperature

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1. Introduction

Osmotic dehydration is a process which reduces the water activity (a_w) of foods (mainly fruits) by placing them in contact with a concentrated solution of sugars. It is one of the most suitable methods to increase the shelf life of fruits and vegetables [1] and it is frequently used as a pre-treatment to improve the quality of fruits which will be afterwards dehydrated by air-drying or freeze-drying [2, 3].

Sucrose is used in osmotic dehydration of fruits because of its accessibility and sensory acceptability [4, 5]. But it has certain drawbacks which include non-enzymatic browning, since it can be easily hydrolyzed into reducing sugars (at acid pH) and its low glass transition temperature (T_g) which leads to sucrose crystallization even at low relative humidities (% RH). The use of trehalose instead of sucrose has been proposed to deal with these disadvantages [6].

Trehalose is a non-reducing sugar with a high chemical stability under low pH conditions, therefore, it does not react with amino acids or proteins by Maillard browning reaction [7-9]. T_g of trehalose is much higher than that of sucrose [10-12]; in the anhydrous state the T_g of trehalose is about 105–115ºC as compared to 60–62ºC for sucrose.

Knowledge of the kinetics of water sorption of dehydrated fruits is required to establish optimum conditions for packaging, storage and utilization [13]. However, freeze-dried fruits are non-equilibrium systems because at reduced moisture content they are supersaturated in sugars which may crystallize upon water sorption [10, 14].

It has been reported in the literature that sugars in amorphous food powders have a strong tendency to absorb surrounding water vapor. Once water is sorbed, the T_g of the powders decreases below the storage temperature and crystallization can occur, resulting in the release of sorbed water [14, 15]. The aim of present work was to carefully follow sorption behavior of dried banana products (Control, Sucrose added and Trehalose added) over a period as long as 100 days in order to detect any sugar crystallization which would be reflected in loss of moisture content.

2. Materials and Methods

Sample preparation and osmotic dehydration

Ripe bananas (*Musa sapientum,* from Ecuador) were peeled and cut into uniform slices (5mm thick, average diameter of 3cm) using a vegetable slicer. Slices were placed in a citric + ascorbic acid solution (0.5%, 0.25% w/v, respectively) for two minutes to retard enzymatic browning. Two different osmotic dehydration (OD) solutions were used: 45% (w/w) sucrose (Ledesma., Argentina) and 45% (w/w) trehalose (Ingredion, Argentina). Concentration used corresponded to the solubility limit of trehalose [16]. A fruit:solution ratio of 1:3 was used without agitation and samples were kept in 1L containers at room temperature (20 ± 2 ºC) during six hours [17]. Then, banana slices were taken out from the osmotic medium, gently dried (with paper towels) to remove the excess of solution, placed on a drying tray (30 slices per tray for freeze-drying batch) and freeze-dried. Total soluble solids (ºBx) were measured before and after the OD procedure.

Freeze drying

A tray of banana samples (30 slices) was placed for 24h in a freezer at -20ºC. It was afterwards freeze-dried in a FIC Ll-I-E300-CRT freeze-dryer (FIC, Rificor, Argentina) operated with a freezing plate at -35°C. Once a vacuum below 200 µmHg was obtained (after 4 hours), the freezing plate was turned off and the drying process continued at room temperature (around 20 ºC) for a period of 40 hours.

Following freeze-drying three different kinds of samples were obtained: 1) Freeze-dried banana without osmotic treatment (named Control), 2) Freeze-dried banana with previous osmotic dehydration in sucrose (named Sucrose) and 3) Freeze-dried banana with previous osmotic dehydration in trehalose (named Trehalose).

Total soluble solids measurement (ºBx)

Total soluble solids (ºBx) content was determined in order to follow the evolution of the osmotic treatment. Samples were crushed into a paste before and after the osmotic treatment and °Bx were measured using hand refractometers (Model N-2 and Model N-3E, Atago, Japan). All measurements were made in triplicate and the average is reported.

Water activity

Water activity (a_w) was determined using an electronic dew point water activity meter Aqualab series 3 (Decagon Devices, Pullman, USA) operated as described in a previous work [16].

Measurement of water sorption

After freeze-drying, samples were milled and transferred into vacuum desiccators and kept at 36ºC (± 1ºC) over saturated salt solutions which provided constant relative humidity between 11 % and 49 % [18].

Water uptake by the different systems (Control, Trehalose and Sucrose) was determined periodically by changes in weight. Final equilibrium conditions were considered to be reached when the difference in weight of samples at intervals of three days was arbitrarily less than 0.0005 g [18]. Three replicate samples were used at each %RH and the average is reported.

Moisture content was determined by first drying the samples in desiccators over magnesium perchlorate at 36ºC followed by oven drying at 103ºC for 6 hours.

3. Results and discussion

As shown in **Table 1**, after osmotic treatment in both sugars (trehalose or sucrose) banana samples had the same ºBx and final a_w; this was expected since both sugars have identical a_w lowering ability [16].

Table 1 – Variation of °Bx and a_w in banana slices before and after osmotic treatment for 6 hours in 45% (w/w) sucrose or trehalose solution at room temperature.

Sample*	°Bx (initial)	°Bx (final)	a_w (initial)	a_w (final)
Control	21 ± 1	-	0.970 ± 0.003	-
With Trehalose	21 ± 1	27 ± 2	0.976 ± 0.003	0.965 ± 0.003
With Sucrose	21 ± 2	28 ± 1	0.977 ± 0.003	0.966 ± 0.003

Moisture uptake and “equilibrium”

The course of moisture uptake with time at low RH % (11 % and 22 %) at 36ºC is shown in **Figure 1** a-b. The sorption behavior of all three systems was similar: after reaching a maximum, moisture content remained almost constant for up to 100 days, although very small changes with time were still observed. It is noteworthy that few researchers study the adsorption behavior of dried fruits for a long time as it was done in present work. Falade and Awoyele [19] studied the adsorption isotherms of fresh and oven-dried bananas (using the same gravimetric-static method) but followed kinetics only up to 14-17 days; after that time-period they considered equilibrium was reached. Tsami et al. [20] also used a relatively short time (15 days) for determining water sorption isotherms of different fruits.

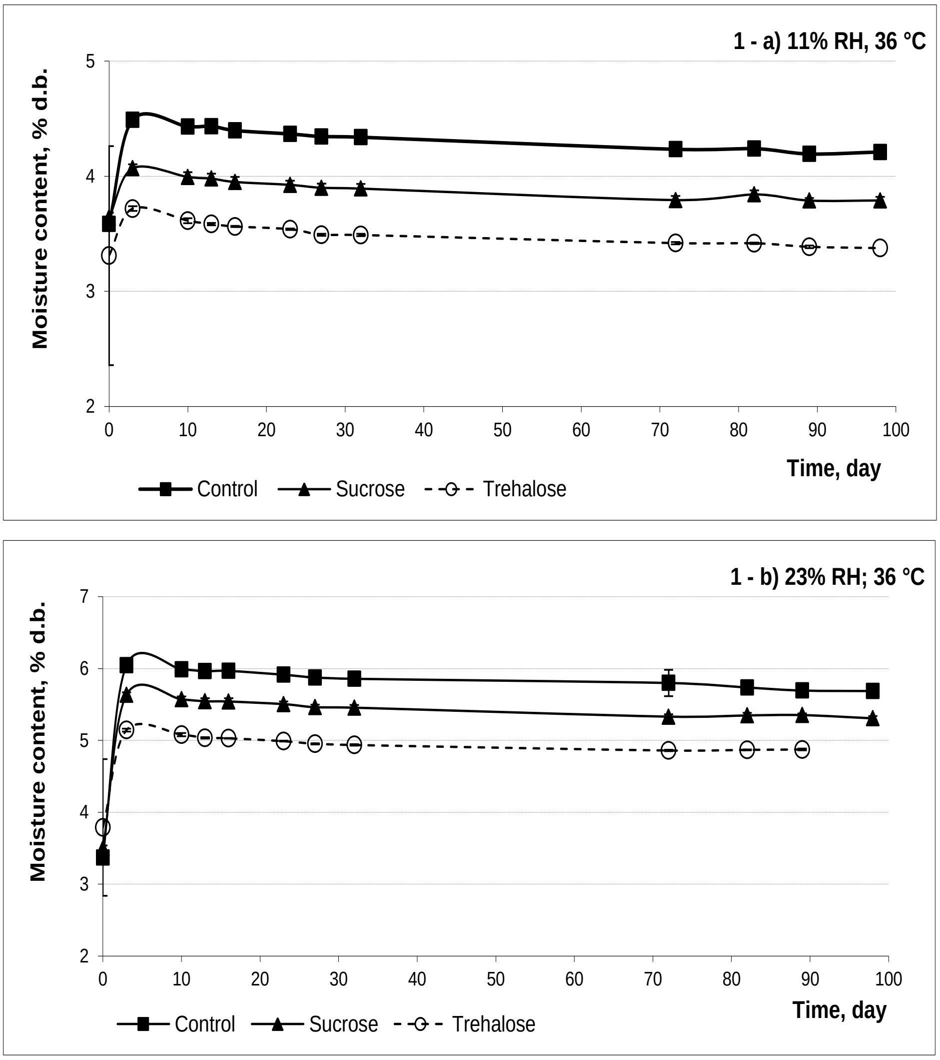

Figure 1 (a and b). Kinetics of water sorption at 36°C at 11 and 22% relative humidity of freeze-dried banana previously osmotically dehydrated with sucrose or trehalose. Standard deviation bars overlap with data points.

Moisture loss and sugar crystallization

At 33 % RH (**Figure 2 a**) Control and Sucrose banana samples reached a maximum moisture content (around 9% dry basis) but then a progressive loss of moisture was observed from day 12 for Sucrose and from day 30 for Control. This was not observed in the Trehalose sample.

The behavior of freeze dried banana Control and Sucrose at 11, 22 and 33 % RH had a striking similarity with the classical work of Makower and Dye [21] on crystallization of amorphous sucrose and glucose exposed to RH ranging from 4.6 to 33.6 % at 25ºC. They found that at low relative humidities, moisture equilibrium was attained and practically no crystallization occurred in nearly 3 years. At higher humidities sugar crystallization with subsequent release of moisture took place. More recently, Yu et al. [22] studied the moisture sorption behavior of freeze-dried amorphous sucrose using a dynamic humidity generating instrument (instead of a gravimetric static method). They also reported moisture-induced sucrose crystallization and that crystallization onset time decreased as %RH increased. Harnkarnsujarit and Charoenrein [15] studied sugar crystallization in freeze-dried mango powder stored at various RH and also reported sugar crystallization revealed by the loss of sorbed water in the water sorption experiment. X-ray powder diffraction and scanning electron microscopy were used to confirm the crystallization. Their results also showed that increased %RH resulted in higher sugar crystallization. The loss of adsorbed water due to sugar crystallization during storage at given %RH, had also been reported previously for other food powders, such as milk powders [23].

As also shown in **Figure 1** a and b, banana osmotically treated with trehalose did not experiment moisture loss in the time-period studied (100 days); this was likely due to the contribution of trehalose to the increase of glass transition temperature (T_g) of the system, as compared to sucrose.

Figure 2a also shows that the rate of moisture loss was higher in banana osmotically dried with Sucrose than in banana Control, which may be attributed to the different relative sugar composition of these systems. In ripe banana, glucose and fructose constitute about 80% of sugars and the rest is sucrose. In sample Sucrose, relative amount of sucrose is likely to increase due to sugar gain from the osmotic bath while glucose and fructose may be leached out. **Figure 2b** shows that all samples evidenced moisture loss when exposed to 43%RH. However, Iglesias et al. [18] showed that amorphous trehalose absorbs water with increasing RH, but the absorbed moisture levels out at 43%RH (i.e. the isotherm presents a plateau). The moisture content at this plateau is close to the amount of water needed to form the dihidrate (10.5% on dry tehalose basis) suggesting crystallization of trehalose. Consequently, the observed moisture loss at 43%RH must be attributed to the crystallization of other sugars present in banana, a phenomenon which is facilitated by trehalose crystallization which no longer contributes to increasing the T_g of the system. **Figure 2c** shows that at a slightly higher RH (49%) there was a similar behavior.

As previously mentioned, weight changes were monitored up to 100 days and a weight difference of 0.0005g between two consecutive measurements was arbitrarily set as equilibrium condition. However, although this condition was approached, it was not entirely reached in many cases (*quasi-equilibrium* condition); this was likely related to very slow sugar crystallization with associated moisture loss over time.

It is generally accepted that sugar crystallization is a time-dependent phenomenon which is a strong function of the difference between storage and glass transition temperatures (T_0-T_g), where T_0 is storage temperature [24]. However, in complex systems (like banana) crystallization does not depend only on T_0-T_g but also on interactions between the amorphous sugars and biopolymers present, as clearly demonstrated by several authors [14, 25]. Iglesias and Chirife [14] reported that in humidified freeze-dried model systems containing different biopolimers (alginate, starch, etc) crystallization of amorphous sucrose was strongly delayed in comparison to pure amorphous sucrose.

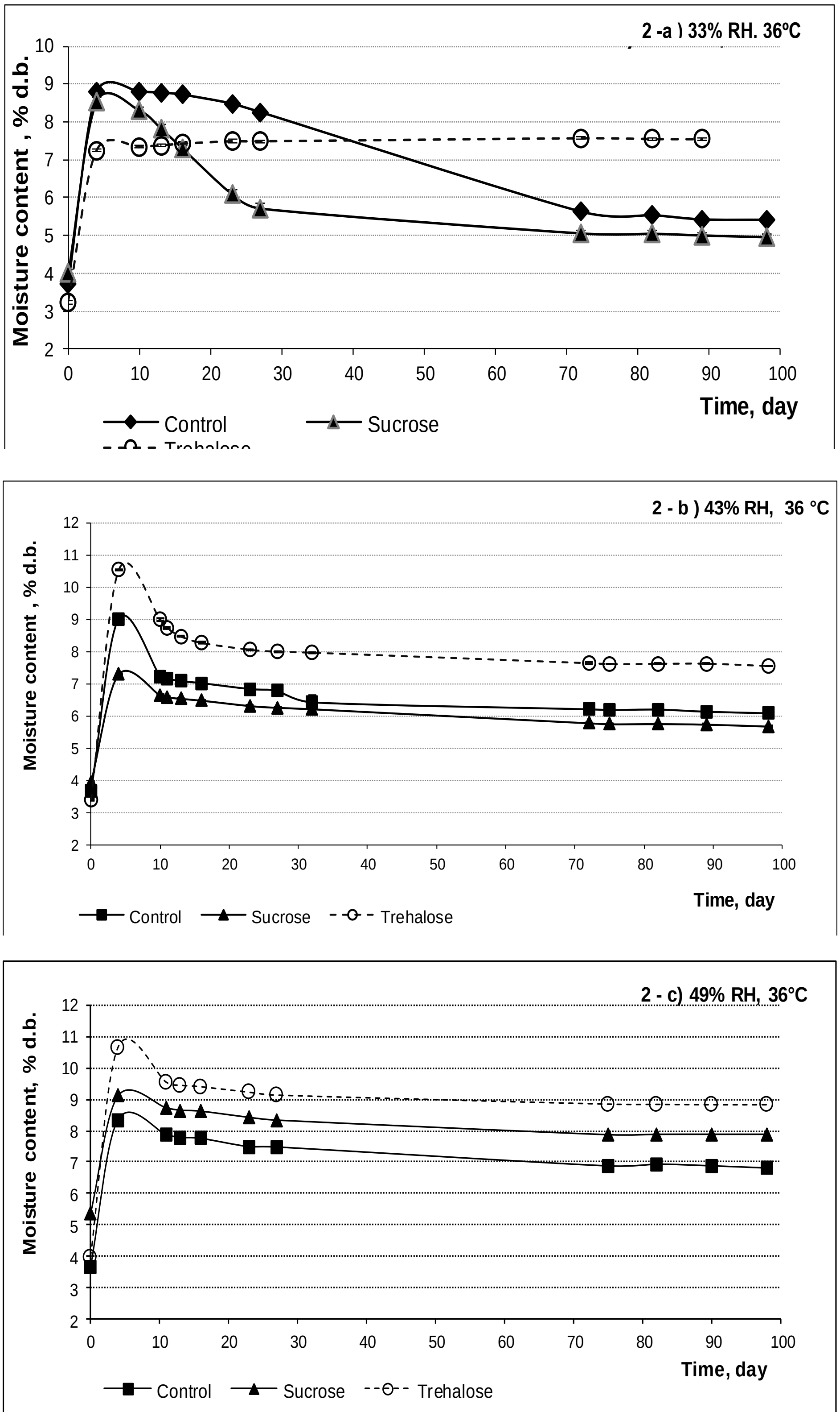

Figure 2, (a, b and c). Kinetics of water sorption at 36°C at 33, 43 and 49% relative humidity of freeze-dried banana previously osmotically dehydrated with sucrose or trehalose. Standard deviation bars overlap with data points.

Analysis of results from T_g values from literature

Moraga et al. [26] reported a T_g value of 41.6 ºC for freeze-dried banana at 11%RH. At the same %RH, Roos and Karel [27] and Iglesias et al [18] reported values of 37.4 ºC and 65.0 ºC for T_g of amorphous sucrose and trehalose respectively. All these T_g values are above storage temperature (36ºC), which explains the observed lack of crystallization in the systems showed in **Figure 1 a**.

T_g values found in the literature for dried banana at 23%RH range between 21 - 30ºC [26, 28]; and for pure amorphous sucrose at the same %RH, it is of 28ºC [27]. These values would tend to predict crystallization; however, since crystallization is a time-dependent phenomenon, T_0-T_g should be above 10ºC to observe crystallization in a reasonable time period [29]. For amorphous trehalose at 22% RH, Iglesias et al [18] reported a T_g value of 45ºC which would partially explain the lack of crystallization during storage at 36ºC (**Figure 1 b**).

At 33% RH, T_g of freeze-dried banana was reported around 8ºC [26] while for pure amorphous sucrose it was around 13ºC [27]; these values would explain the rapid crystallization for banana Control and Sucrose samples observed at this % RH (**Figure 2a**). At this same % RH pure amorphous trehalose has a T_g of 34ºC [18] which would explain the observed lack of crystallization. As mentioned before, at 43%RH (**Figure 2 b**) T_g of trehalose decreases to 14ºC and its crystallization can take place, forming the dihydrate (Tr.2H_2O). After crystallization, trehalose is not able to inhibit the crystallization of other sugars present in banana.

The loss of sorbed water in the freeze-dried banana samples (Control, Sucrose and Trehalose) was attributed to crystallization of sugars other than trehalose. Sugars in these products are usually present in the amorphous state and have a strong tendency to absorb surrounding water vapor. Once water is sorbed, the T_g of the powders decrease below the storage temperature and crystallization can occur, resulting in the release of sorbed water. Trehalose does not release water upon crystallization since it forms a dihydrate. These changes were adequately explained by literature T_g values of related systems (freeze-dried banana, amorphous sucrose and amorphous trehalose).

4. Conclusions

The use of trehalose instead of sucrose in the osmotic bath gave an important technological advantage; these freeze-dried samples crystallized at higher %RH than either simple banana or that osmosed in sucrose.

It was also observed that all water sorption data approached but did not entirely reach equilibrium values; in fact moisture content still changed (decreasing) very little with time, and this was attributed to slow crystallization. This stresses the importance of using long equilibrium times when determining adsorption equilibrium in dried fruits containing amorphous sugars likely to crystalize.

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