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Glass transition changes during osmotic dehydration

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Abstract

The changes in Ataulfo mangoes (*Mangifera índica L.*) osmotically dehydrated were evaluated through Modulated Temperature Differential Scanning Calorimetry (MTDSC) in order to determine their thermodynamic behavior due to water loss (*WL*) and solid gain (*SG*) during the process. These values were related with the effective diffusion coefficients for water (D_{ew}) and solids (D_{es}) into the fruit. The samples were analyzed under frozen conditions. The glass transition temperature (*Tg*) corresponding to sucrose in concentrated solution, and the value referred as *Tg´* for freeze sucrose solutions were founded. Mango *Tg* variation was in increasing with the *WL* decrement, and the melting enthalpy increase with the soluble solids increment into the fruit. As moisture content decrease by dehydration, the food matrix became more viscous and the water and solids transfer are delayed; these changes were reflected in the decrease of effective diffusion coefficients, D_{ew} and D_{es}, while *Tg* in mango samples increase. All these results show the useful with the MTDSC analysis to follow the osmotic dehydration inside the product.

Keywords: Glass transition; heat capacity; diffusion coefficients; osmotic dehydration; mango.

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1. Introduction

The physical state of materials is governed by phase transition, so its knowledge is important in determining the process, storage and consumption conditions. In dehydrated foods, the solid matrix, formed by food polymers and other compounds, may be in an amorphous metastable state (very viscous glass or more liquid-like rubber), which is very sensitive to changes in temperature and moisture. The change from the glassy to the rubbery state occurs as a second order phase transition at a temperature known as the glass transition temperature (*Tg*). The consequence of phase transitions is the molecular mobility change that is in relation with diffusional and mechanicals properties [1, 2].

The osmotic dehydration (OD) is a partial dehydration technology applied to high water content foods, by osmotic solution immersion (OS), which not damage fruit texture, like mango. This effect can

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be explained by the sugar cryoprotective function in the fruit tissue. The low moisture foods are usually solid materials with glassy structure that can become plasticized as a consequence of water content or temperature increase. Mostly, the food amorphous state can be achieved by a rapidly water elimination. This transition, from glassy to rubbery state, is a kinetic transition that can be measured by heat capacity (*Cp*) changes, by a drastic change in molecular rotational mobility or by an abrupt change in hydrogen bonding [3, 4]. With MTDSC technique is possible to obtain complex heat capacity information, in isothermal as well as in non isothermal conditions, originating the heat flow signal decomposition on its reversible and irreversible contributions, allowing the study of complex systems [5].

A tendency to explain the foods processing and storage behavior, is considering them like water plasticized polymeric systems. In this sense, the Gordon and Taylor model allows to predict the binary mixes *Tg* value and the water plasticizer role from the pure compounds *Tg* [6].

Transformation, storage and quality of foods are fundamental physicochemical process based on the transport and equilibrium state of water into the system. These can be the water diffusion into food or the moisture exchange between food and the environment. It is known that water concentration significantly affects the diffusion coefficient, due to its dependence with the food physical structure.

Thus, the aim of this study was to evaluate the *Tg* changes by MTDSC, under frozen non isothermal conditions, during Ataulfo mangoes (*Mangifera índica L.*) osmotic dehydration in a 45% sucrose solution at 60 ° C. It was also possible to obtain melting temperature (*Tm*) and changes in heat capacity (*Cp*) and enthalpy (*ΔH*) into the fruit. These values were related with the effective diffusion coefficients for water (D_{ew}) and solids (D_{es}) computed from Fick´s second law analytical solution.

2. Materials and Methods

Mango cubes (1 cm^3) were dehydrated in 45° *Bx* sucrose solution at 60° *C* for three hours. Samples were taken every 30 minutes in order to analyze its weight and moisture content. The Brix index of the pressed mango cuts was measured using a digital refractometer (Sper Scientific 300003, AZ, U.S.A.). The total moisture content was determined by placing the sample in an oven at 60° *C* until constant weight.

Then water loss (*WL*) and solid gain (*SG*) during the process were computed as follows [7]:

$$WL = \frac{(ww_0) - (w_t - ws_t)}{(ws_0 + ww_0)} x100 \tag{1}$$

$$SG = \frac{(ws_t - ws_0)}{(ws_0 + ww_0)} x100 \tag{2}$$

where ww_0 is the weight of water and ws_0 is the weight of solids initially present in the fruit; w_t and ws_t are the weight of the fruit and the weight of solids at the end of treatment, respectively. Both parameters are expressed as *g/100g* of fresh sample.

The solution of Fick's second law for diffusion from a rectangular parallelepiped, when all their sides are equal (*2a = 2b = 2c*), result in the equations 3 and 4 for the transfer of water and solute in a cubical configuration, respectively [8, 9]:

$$Mr = \frac{m_t - m_\infty}{m_0 - m_\infty} = \sum_{n=1}^{\infty} C_n^3 exp\left[-D_{ew} t q_n^2 \left(\frac{3}{a^2}\right)\right] \tag{3}$$

$$Sr = \frac{s_t - s_\infty}{s_0 - s_\infty} = \sum_{n=1}^{\infty} C_n^3 exp\left[-D_{es} t q_n^2 \left(\frac{3}{a^2}\right)\right] \tag{4}$$

where *Mr* and *Sr* are the moisture and solute ratio; the subscripts 0, ∞ and t represent the relevant concentrations initially, at equilibrium, and at any time; C_n is equal to $2\alpha(1+\alpha)/(1+\alpha+\alpha^2 q_n^2)$ where q_n's are the non-zero positive roots of the equation $\tan q_n=-\alpha q_n$. Here, α is the ratio of volume-solution of each piece. For short times, the diffusion coefficients were evaluated from the slope of $-\ln(Mr/C_1^3)$ and $-\ln(Sr/C_1^3)$ *vs.* time [10], under limit conditions: $C=C_0,\ t=0,\ -l<x<+l$ and $C=C_1,\ t>0,\ x=l$.

In the other hand, a mass fraction of each sample (≈16 *mg*) was placed in hermetic aluminum pans in a MTDSC 2920 (TA Instruments, NJ, U.S.A.). After stabilization at -50° *C*, the samples were heated to 40 °*C* at 5°*C/min*. The *Tg* range was evaluated as well as the ice melting enthalpy (ΔH), the melting point (*Tm*) and *Cp* changes in each thermogram by the Universal Analysis software. The ratio of this enthalpy by the pure ice fusion enthalpy was the amount of unfrozen water (*Wg´*). The freeze-concentrated solution in the fruit (*Cg*) was obtained by extrapolating to zero the fusion enthalpy as a function of the Brix index [11].

Gordon and Taylor empirical equation was used to predict *Tg* as a function of water content:

$$Tg = \frac{x_s Tg_s + k x_w Tg_w}{x_s + k x_w} \tag{5}$$

where *Tg*, Tg_s, and Tg_w are glass transition temperatures of the samples, solid matrix and water, respectively, x_s and x_w the corresponding percent of solid and water contents and *k* (4.7) an empirical parameter [1]. Glass transition temperature of pure water was taken as Tg_w = -135° *C*.

Also the diffusion coefficients were computed as a function of time by the model proposed by Azuara, et al. (1992) [12].

3. Results & Discussion

Dehydration kinetics, for water and soluble solids, and the osmotic parameters are shown in fig. 1. Water loss and solute gain were higher in the initial phase of osmosis. With progression of time, the osmotic driving potentials for moisture and solute transfer decreased. This may be due to structural changes caused by the rapid loss of water and uptake of solids near the surface, leading to compaction of these surface layers and increased mass transfer resistance for water and solids. Also, the progressive solid uptake might have been resulted in the formation of high solids subsurface layer, which interfered with the concentration gradient across the product–solution interface and acting as a barrier against removal of water and uptake of solids [13]. It can be seen that the product loss 64% water and gain 26% solids approximately during the process.

Since dehydration only was carried out by three hours, rates of change in moisture content *(-dm/dt)* and solids (*ds/dt*) were obtained as a function of the average moisture and solids content, respectively, to predict equilibrium values: M_∞= 0.492 and S_∞= 0.464. Effective diffusion coefficients for solutes (D_{es}= 1.694×10^{-10} m^2/s) and water (D_{ew}= 2.62×10^{-10} m^2/s), were computed by analytical solution of Fick´s second law. The water diffusion is higher than solids, where the driving force behind the mass transfer is the osmotic pressure difference. Mass transfer rates of water and solutes occurred through diffusional/osmotic mechanisms in the intercellular spaces or trans-membrane tissue. In solid uptake the observed effects in mango may be explained through the great influence of solution viscosity on the gain by hydrodynamic mechanisms in the tissue pores. The different induced viscosity in the free liquid phase occupying intercellular spaces will affect the diffusion component in this non-compartmented volume and so, the overall D_e value [14].

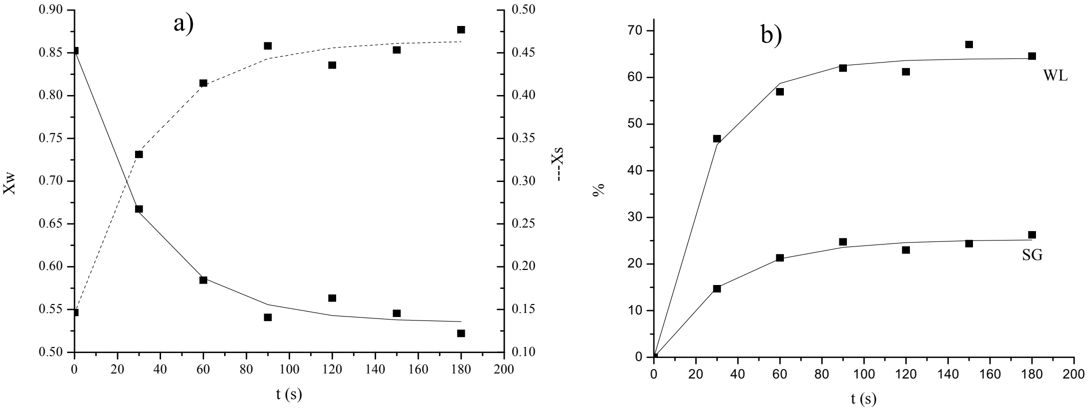

Fig. 1. Water and solid kinetics (a) and osmotic parameters (b) during mango OD

Figure 2 shows the MTDSC thermograms at each osmotic dehydration time, where can be seen that the T_m decrease as a function of time and water content. The ice fusion enthalpy also decrease when the sucrose concentration into the fruit increase because there is less freezing water (table 1). The onset melting temperature is defined by the intersection of the tangent to first part of MTDSC melting peak and the extrapolated baseline before melting; the enthalpy is the peak area. The small endothermic peak observed for high moisture contents immediately before fusion is known as antemelting [15] and has been observed during phase transitions of biological products, suggested that it is due to molecular layers of liquid which form in the crystals surface; another explanation for antemelting endothermic peak could be the formation of limited region of an eutectic mixture, melting at lower temperatures.

In frozen sucrose solutions, it is known that the lower temperature step change (T_1) is the primary glass transition of the amorphous sucrose phase, and this transition temperature and peak height will change with cooling rate and sucrose concentration [16], but can also lead to changes in the appearance and position of the events as the viscosity of the solution increases. So the founded values may correspond to the OS bound water adsorbed in the solid matrix (Tg_{sucrose} in table 1). Luyet and Rasmussen (1968) defined the event occurring at T_1 as Tg for sucrose solutions and describe two events occurring on either side of the midpoint for T_2 as antemelting or an incipient melting of ice. They observed that these temperatures were independent of the starting concentration for the solutions [16]. The Tg' in table 1 seems to be the antemelting of ice crystals, because in the latest processing times there is not presence of this transition due to the incipient melting peak.

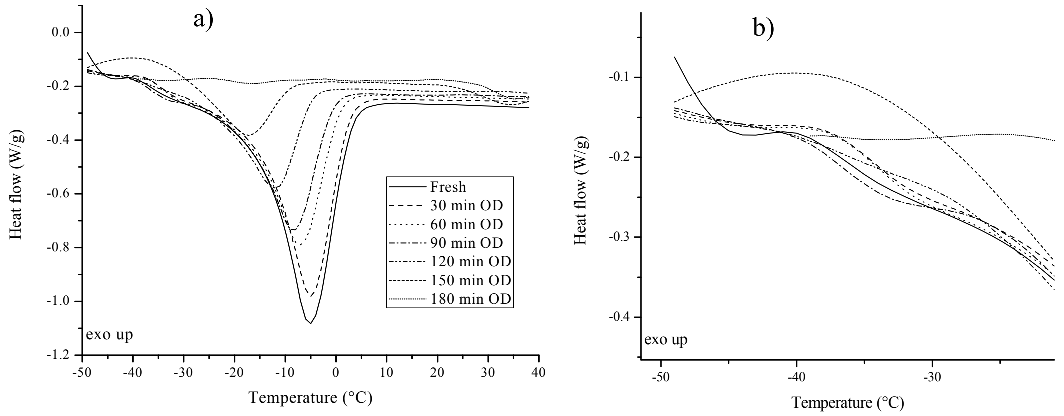

Fig. 2. MTDSC thermograms during mango OD (a) and endothermic peaks on glass transition region (b)

Although freezable water is present in samples, the crystallization process was progressive inhibited probably due to the increasing viscosity of the product liquid phase, by the major solid concentration in the amorphous matrix. At high water contents, a change in the physical state of carbohydrates from an amorphous to a crystalline form may occur. Crystallization of amorphous sugars results in the loss of adsorbed water if anhydrous crystals are formed as occurs with sucrose [18, 19]. This water content enclose un-freezable water mass fraction (*Wg´*) which is the amount of water remaining unfrozen even at very low temperature. It includes both un-crystallized free water and bound water adsorbed in the solids matrix. Also, in table 1 can be seen the glass transition of the solids matrix in the frozen sample (*Tg*) which was determined by MTDSC; these values are due to the formation of a same solid matrix associated to un-freezable water and transformation of all free water into ice although the sample contains different level of total water before scanning.

Table 1. Values obtained from MTDSC at different solid content (°Bx) during mango OD process

t *(min)*	°Bx	Xw	a_w	Tm *(°C)*	H *(J/g)*	Tg *(°C)*	ΔCp *(J/g/°C)*	$Tg_{sucrose}$ *(°C)*	Tg´ *(°C)*	Wg´
0	18.0	0.852	0.94	-5.19	-148.5	-35.41	0.440	-46.39	-12.13	0.430
30	32.5	0.667	0.79	-4.96	-131.8	-33.74	0.515	-45.14	-10.67	0.322
60	35.5	0.584	0.70	-7.08	-108.4	-33.41	0.517	-44.84	-14.97	0.243
90	39.5	0.541	0.66	-8.43	-106.3	-35.35	0.557	-44.68	-15.10	0.216
120	41.5	0.563	0.68	-11.93	-70.3	-39.14	0.440	-46.26	-18.68	0.172
150	42.5	0.546	0.66	-17.50	-40.8	-30.49	0.215	-53.79	-	0.121
180	43.0	0.522	0.64	-16.58	-1.5	-24.97	0.812	-45.36	-	0.005

The second order transitions (glass transitions) were identified in the derivative heat flow signal, as an endotherm, and the heat capacity changes (*ΔCp*) associated were obtained from the increase in the reversible *Cp* signal (fig. 3). All reported values correspond to the transition midpoint. Around 120 min OD the *ΔCp* are due to structural changes, as seen on reversing *Cp* signal, where the most important variation on fusion zone are representatives of structure changes and water-sucrose interactions. So that represents a good stability parameter.

As expected, the *Tg* is a direct relationship of water activity, due to the water plasticization at high moisture content (fig. 4). During the osmotic treatment there is always a leaching of solutes from the solid sample and its impregnation with solutes from the solution. In this case it is expected an increase of the relative amount of sucrose with the corresponding shift of *Tg* and *Tg′* curves during OD process. It can be postulated that the founded *Tg's* are a result of sugar left behind after water removal by dehydration.

Figure 4 shows the dependence of *Tg* (represented by the Gordon–Taylor equation) and effective diffusivity (represented by the Azuara′s model [12]) on moisture content. The moisture content at which the samples presents a change from the glassy to the rubbery state, at room temperature (≈20° *C*), was identified as the critical moisture content (*Cg′*), or as the concentration of the freeze-concentrated solution in the fruit (*Cg*), and it was predicted to be 56% using the Gordon and Taylor equation. Above this value, dehydrated mango become sticky and the crystallization of amorphous compound could take place. At this critical value, a_w of sample was around 0.68 and the corresponding critical solid diffusivity (Dg_s) was 2.759x10^{-9} m^2/s and for moisture (Dg_w) 5.160x10^{-9} m^2/s. Solids effective diffusivity increased sharply as mango experiment glass transition, due to a mobility increase facilitated by an increase in moisture content. This transition occurs around 120 min OD process as can be seen in MTDSC thermogram and in the momentary moisture increment, due to structural changes.

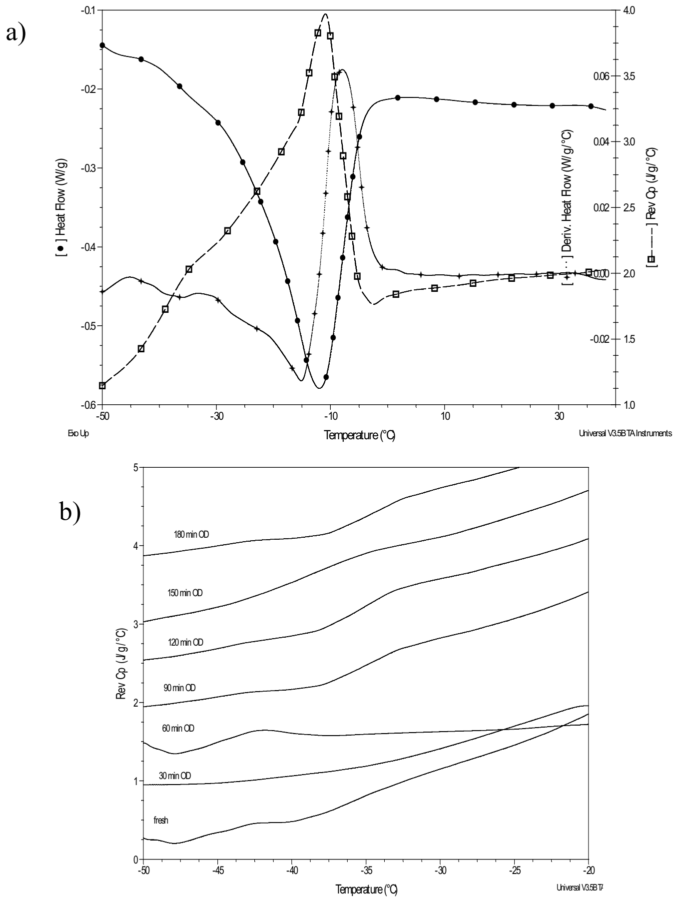

Fig. 3. *Tg* range identification (120 min OD) by heat flow signal deconvolution (a) and heat capacity changes determination in reversible *Cp* signal for each time during mango OD (b)

Barat, et al. (2001) [22] explains that from a determined dehydration level, the cell collapse is impeded by the rigidity of the cell matrix which is imposed by cell bonding zones. In this case intercellular spaces increase their volume at the same time as the cells lose water and volume. At this moment, pressure of the internal gas is decreasing, and a pressure gradient appears between internal volume and solution. This will lead to external liquid penetration through the pores, the efficiency of which depends on the pressure drop during liquid inflow.

The glass transition affects diffusion-controlled chemical reactions through the decrease of diffusion coefficient. The decrease in diffusivity is due to the changes in viscosity and mobility. The water diffusion coefficient in low-moisture food polymers decreased with the decrease of moisture content without any break in the glass transition when plotted diffusivity versus water content. However, the solid gain by the product during OD in the presence of a certain amount of water has a more plasticizing effect on products rich in sugar, hence suppressing the glass transition temperature, showing as an inflexion point. The diffusivity depends mainly on moisture content and exhibits a low sensitivity to the nature of surrounding polymer. The decrease of diffusivity near or below glass is not solely due to the decrease of viscosity. Other factors affecting diffusivity are the porosity, porous structure, size (solute and matrix) of molecules, nanodefects, and structural collapse of foods [20].

4. Conclusion

Even though the osmotic dehydration seems a very promising process, the industry is not implementing it as widely, due to the poor characterization of the internal changes in the food product.
As can be seen the water activity is not the main food stability parameter, because the presence of small amounts of water in products with high sugar content has little influence on it. However, the knowledge of *Tg*, *Cg*, and *Dg* is also very important since they define the point of dynamics stability and, as a consequence, the diffusion mechanisms change.

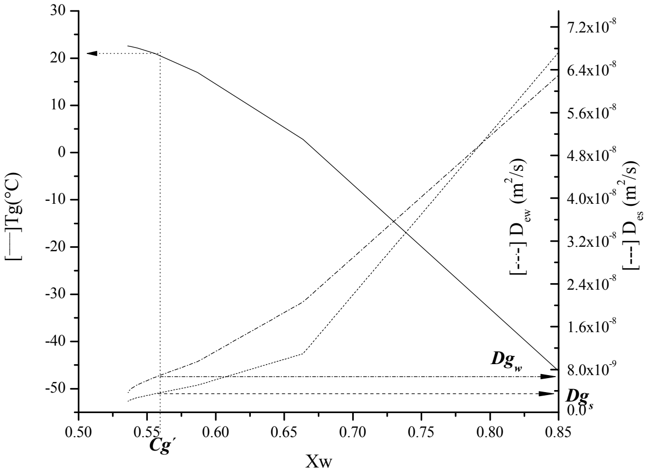

Fig. 4. Dependence of *Tg* (Gordon –Taylor) and effective solids diffusion coefficient on moisture content

MTDSC is a very sensitive analytical method to define the thermodynamics of physico-chemical modifications in food during its transformation and storage, which must have more application. The *ΔCp* maybe is the most important stability parameter, since represents structural as well as kinetic phenomena.
Simultaneous microstructure studies are necessary to confirm the results obtained by MTDSC. Also, the use of other analytical techniques, like FTIR or NMR, is desirable to study the product molecular changes

during OD in order to obtain more information about this kind of process to become an industrial operation.

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