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Physico-Chemical and Mechanical Properties of Apple Disks Subjected to Osmotic Dehydration and Different Drying Methods

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Abstract The effect of sucrose infusion (SI) pretreatment and dehydration methods (freeze and air drying) on physical and textural properties of apple disks were analyzed. Dried samples were humidified between 11% and 43% relative humidity (RH) at 20 °C. Control samples (air- and freeze-dried) behaved similarly regarding water sorption and glass transition temperature. SI process caused important changes in the water sorption behavior of air-dried samples. Nuclear magnetic resonance relaxation times values (T_2) for freeze-dried apples were higher than those for air-dried samples. Samples subjected to previous SI always presented lower T_2 values because they had lower water contents. The dehydration method also affected the mechanic behavior. Air-dried samples exhibited higher F_{max} values during puncture assay than those obtained for freeze-dried samples. SI samples showed higher F_{max} values for both drying methods. The crust formed during air drying generated crispier materials along the whole RH range, while freeze-dried matrices were more deformable with the increase in RH. SI pretreatment also allowed diminishing browning development. The results obtained are useful in the choice of processing technologies of organoleptically acceptable dehydrated fruits for direct consumption or for their incorporation into compound foods.

Keywords Apple · Dehydration · Physical properties · Texture · Sucrose infusion

Nomenclature

AD	Air-dried
a_w	Water activity
FD	Freeze-dried
F_{max}	Maximum force obtained in the puncture assay (kgf)
RH	Relative humidity (%)
SEM	Scanning electron microscopy
SG	Sugar gain (% *w*/*w*)
SI	Sucrose infusion pretreatment ($SI_{0.85}$ and $SI_{0.92}$ correspond to sucrose infusion pretreatments in which the fruits reached equilibrium a_w values of 0.85 and 0.92 respectively).
SI-AD	Sugar infused and then air-dried fruits
SI-FD	Sugar infused and then freeze-dried fruits
T_2	^{1}H NMR spin–spin relaxation time (μs)
T_g	Glass transition temperature (°C)
WL	Water loss (% *w*/*w*)

CIELAB parameters

L^*	Luminosity
a^*	Redness–greenness
b^*	Yellowness–blueness

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Introduction

Fruits and vegetables are highly recommended as part of the diet due to their nutritional value and health-promoting effects. Apple pomace, the most important temperate fruit of the world, is consumed not only as fresh but also as processed food in the form of jam, marmalade, juice, and dehydrated products (Lu and Foo 2000; Shyu and Hwang 2001; Taiwo et al. 2001). Argentina's apple production (1.8 million tons/year) is mostly concentrated in the Patagonia region. More than 50% of the crop goes to the processing industry due to the scarce Argentine supply of the varieties most demanded by international customers and to the high percentage of fruit failing to meet the fresh market quality standards. Eighty percent of the processed volume is crushed to obtain juice concentrate (Bruzzone 2006; Moavro 2010). In this context, it is desirable to seek novel, attractive, and high quality products from apple fruits to widen product availability and diversify the market.

Fruit drying is a well-known preservation method, mainly because water removal and water activity lowering reduce the risk of microbial development. Dried fruits are widely used as ingredients in many food formulations such as pastry, confectionery products, ice cream, frozen desserts, and yogurt (Mandala et al. 2005). In recent years, much attention has been paid to the quality of foods during drying. Both the method of drying and the physicochemical changes that occur in tissues during drying may affect the quality of the dehydrated product (i.e. Askari et al. 2006; Funebo et al. 2000; Jaya and Durance 2009; Khalloufi and Ratti 2003; Krokida et al. 2001; Lombard et al. 2008; Ochoa-Martínez et al. 2006; Mujumdar and Law 2010).

Freeze drying provides high-quality porous products, bearing high aroma retention and good rehydration properties (Le Loch-Bonazzi et al. 1992). Drying at high temperatures and long times may cause damage in the nutritive and sensorial characteristics, affecting flavor, color, and nutrients of dried food (Lenart 1996; Lin et al. 1998). A way of producing dried fruits of good quality is to use predrying treatments, which allows obtaining products with characteristics organoleptically more similar to the original fresh products. A sugar infusion, applied as a pretreatment, can significantly affect the water and solute exchange, allowing a partial depression of water activity before the dehydration step. This osmotic process also allows to infuse into the product not only the solute used to control water activity (mostly sugars in the case of fruits) but any solute for improving sensory and nutritional quality (antibrowning agents, bioactive compounds or agents for improving or maintaining firmness and for pigments stabilization). Thus, it is possible to change, to a certain extent, the food system formulation, making it more suitable to further processing (Torreggiani and Bertolo 2001). By choosing a suitable method and the appropriate conditions during the second drying step, the final product quality can be controlled.

Product texture is substantially modified during drying. After dehydration, many food products are partially or completely in the amorphous state, which may change from a solid glassy state to a liquid-like rubbery state (Karel et al. 1994; Slade and Levine 1995). In low moisture foods, the glassy state provides a firm and crunchy/crispy texture, which causes a brittle fracture. When these products adsorb water, they lose the crunch and rigidity properties, and the fracture may occur with plastic flow, denominated ductile behavior (Dobraszczyk and Vincent 1999). This deteriorative effect has been associated to the plasticizing effect of water, which reduces the glass transition temperature (T_g) (Ablett et al. 1993; Katz and Labuza 1981; Slade and Levine 1991). While this holds for relatively simple and homogeneous systems, more complex conditions occur when non-homogeneous, multidomain, multi-component systems are concerned (Venir et al. 2007). Dehydrated fruit tissues are complex food materials, consisting of many components and more than a single phase, with properties that may not change at the same time as predicted by the glass transition theory (Peleg 1999). Therefore, the knowledge of the glass transition alone might not be enough to interpret texture changes. Mechanical properties are closely associated with the microstructure developed as a result of deformations (shrinkage/swelling) in cells and intercellular spaces and of rupture of cellular bonds taking place throughout drying process (Contreras et al. 2005; Deng and Zhao 2008). Moreover, ingredients added during processing, such as sugars can affect the structural organization of products and so their interactions with water, which is likely to play a role in mechanical properties of materials and most expectedly in product crispness (Barrett et al. 1994; Onwulata et al. 2001; Roudaut et al. 2002; Van Hecke et al. 1998). The molecular mobility behavior of water and solids can help in the understanding of the changes of the texture characteristics caused by water plasticization. In this sense, nuclear magnetic resonance (NMR) spectroscopy allows water and food solid mobility to be studied independently (Gil et al. 1996; Kalichevsky et al. 1992; Kou et al. 2000). The slowing of water motion in low-moisture samples reflects strong water–solid interactions through hydrogen bonding (Chen et al. 1997), which corresponds to the water molecules that are strongly influenced by their proximity to the solids components.

Enzymatic and non-enzymatic browning are two major concerns during dehydration and storage. In dehydrated systems, non-enzymatic browning is a diffusion-limited reaction due to the mobility restrictions of the reactants; therefore, it can be affected by the glass transition (Buera and Karel 1995).

Hence, the evaluation of the relationship among process factors, product quality (texture and color), water sorption, glass transition, and molecular mobility of solids is of great interest for processing and storage, both for quality control and as a tool to analyze processes to define and optimize an adequate technology for each vegetal matrix. The purpose of this study was to develop dry apple disks with improved properties regarding texture, sweetness, color, and stability, to be incorporated as ingredients into complex foods. To this aim, we evaluated the effect of the application of osmotic dehydration and different drying methods on the physico-chemical and mechanical properties of apple disks after humidification of the dry samples at different relative humidities (RH).

Materials and Methods

Sample Preparation

Raw apples (*Malus pumila*, Granny Smith *var.*; $a_w \cong 0.99$; 10.4–12.2°Brix and pH 3.3–3.4) were obtained from the local market and stored at 4 °C until the moment of the experiments. Apples were washed, hand peeled, and cut into disks (30 mm diameter and 5 mm thickness) parallel to the longitudinal axis of the fruit using a cork borer.

Pretreatment

Before the drying process, the cut material was subjected to a dry sugar infusion treatment (SI) at room temperature, which involved direct mixing of fruit pieces and specific solutes in required proportions. Two systems were prepared using sucrose as humectant to decrease water activity till 0.85 and 0.92 values, respectively. This was achieved by equilibration of the components in the food system (fruit slices and a dried mixture of sucrose, 150 μg/g sodium bisulfite, and 1,000 μg/g potassium sorbate). The amount of sugar and chemical agents was determined according to the weight of the fruit and the final levels required after equilibration of the product. Sucrose concentration in the mixture was calculated using the Ross equation (Alzamora et al. 1993) to attain the a_w equilibration value desired between apple slices and the formed syrup:

$$a_{w\,\mathrm{equilibrium}} = \left(a_w^0\right)_{\mathrm{apple}} * \left(a_w^0\right)_{\mathrm{sucrose}} \quad (1)$$

where $\left(a_w^0\right)_{\mathrm{apple}}$ is the water activity of the fresh fruit (≈ 0.99) and $\left(a_w^0\right)_{\mathrm{sucrose}}$ is the water activity of sugar, both calculated at the total molality of the system.

Potassium sorbate and sodium bisulfite were used as antimicrobial and enzymatic browning preservatives, respectively (Leistner 2000). Reagents were all food grade (Saporiti S.A., Argentina). The a_w in the fruit and syrup was monitored until a constant value was reached; the time to equilibrate the system was 7 days for the samples that reached a_w 0.92 and 10 days for those that reached a_w 0.85. The fruit slices were taken out of the syrup, drained and placed on tissue paper to remove the residual syrup, and then placed in the containers to measure a_w. The syrup was directly placed in the containers to measure a_w. Final water activity values achieved after infusion process were selected in order to have dried fruits of different levels of sweetness, as well as to study the impact of sugar concentration on the analyzed properties. After equilibration, slices were taken out of the generated syrup, drained and placed on tissue paper for the removal of the residual syrup left on their surfaces, and were subjected to further dehydration processes. Dehydrated apples with pretreatment were compared with no pretreated ones (controls) and subjected to the same humidification conditions.

Drying Methods

Two different drying processes were used:

(a) Freeze drying: apple disks were quenched with liquid nitrogen right after cutting for control samples and after pretreatments for the rest of the samples. The freeze drying process lasted 48 h. A freeze drier Alpha 1–4 LD/ 2–4 LD-2 (Martin Christ, Gefriertrocknungsaniagen GmbH, Osterode, Germany) was used. It was operated at −84 °C at a chamber pressure of 0.04 mbar.
(b) Air drying: an air convection oven was used. Samples were dried for 24 h at 60±1 °C and 10% relative humidity (RH).

Humidification

After drying, apple disks were put into vacuum desiccators over saturated salt solutions in the range between 11% and 43% RH. The salt solutions used were $LiCl_2$ (a_w=0.11), CH_3COOK (a_w=0.22), $MgCl_2$ (a_w=0.33), and K_2CO_3 (a_w=0.43) (Greenspan 1977). The samples were allowed to equilibrate (sample a_w equal to salt solution a_w) for 14 days at 20 °C in order to achieve different moisture levels.

Sample Analysis

Water Content, Water Activity (a_w), and Soluble Solids

The water content was determined (in duplicate samples) gravimetrically, by difference in weight before and after vacuum drying over magnesium perchlorate at 60 °C. Results were expressed as percentage in dry basis (% db). The a_w was determined by dew point using an Aqualab

Series 3 (Decagon Devices, Pullman, WA, USA). Soluble solid content percent in the liquid phase was analyzed by measuring the refraction index in a refractometer (Atago, ABBE DR-A1, Tokyo, Japan) at 25 °C.

Thermal Transitions

Glass transitions were determined by differential scanning calorimetry (DSC; onset values) using a calorimeter model 822 (Mettler Toledo, Schwerzenbach, Switzerland). The instrument was calibrated with indium (156.6 °C), lead (327.5 °C), and zinc (419.6 °C). All measurements were performed at a heating rate of 10 °C/min. Approximately 10 mg of each sample were placed in 40 μl aluminum pans, which in turn were hermetically sealed. An empty pan served as reference. Thermograms were evaluated using Star^e software v. 6.1 (Mettler Thermal Analysis). An average value of at least two replicates was reported.

Molecular Mobility

A pulsed NMR Bruker Minispec instrument model mq 20 (Bruker Biospin GmbH, Rheinstetten, Germany), with a 0.47 T magnetic field operating at resonance frequency of 20 MHz, was used for measurements. Equilibrated samples were removed from the desiccators, placed into 10 mm diameter glass tubes, and returned to the desiccators an additional time of 24 h before analysis. All determinations were performed in triplicate.

The spin–spin relaxation times (T_2) was measured using a free induction decay analysis after a single 90° pulse. The decay envelopes were fitted to mono-exponential behavior with the following equation:

$$I = A\exp(-t/T_2) \tag{2}$$

where I represents protons signal intensity, T_2 corresponds to the protons in the solids and strongly bound water of the sample, and A is the signal intensity of protons in T_2 state.

Since no 180° refocus pulse was used in the experiments, the spin–spin relaxation time constants are apparent relaxation time constants, i.e. T_2^*. However, for solid samples (like ours), we can consider that the intrinsic T_2 is very close to the T_2^* as reported previously by Fullerton and Cameron (1988). Therefore, T_2 was used for convenience.

Color Measurement

Surface color of dehydrated samples was measured by a handheld tristimulus reflectance spectrocolorimeter with an integrating sphere model CM-508-d (Minolta Corp., Ramsey, NJ, USA) with a white background of reflectance provided by the manufacturer. Values were obtained for D65 illuminant and 2 ° standard observer. The L^*, a^* and b^* components of the CIELAB uniform space were recorded, where L^* indicates lightness, a^* indicates chromaticity on a green (−) to red (+) axis, and b^* chromaticity on a blue (−) to yellow (+) axis. Average values of six replicates were reported for each experimental condition.

Mechanical Properties

A puncture assay was performed using a universal assay instrument model 3344 (Instron, Massachussets, USA). A 4-mm cylindrical probe was used at a crosshead speed of 50 mm/min, and force–distance curves were recorded during the test probe. A special test cell was designed so that apple disks were tightly held by a bolted ring while penetrated through the center by the probe (Acevedo et al. 2008). Force–distance curves were recorded, while the probe descended through the apple disk to the point of maximum force at fracture (F_{max}), which was used to evaluate product firmness or hardness. The reported values of F_{max} correspond to the average of individual measurements of ten samples corresponding to each experimental condition. The assay was performed in the range from 11% to 43% RH.

The samples at 43% RH could not be measured with this assay because they were very soft and could not be held in the holding device.

Scanning Electron Microscopy

A scanning electron microscope (Zeiss SUPRA 40 field emission gun SEM, Germany) was used to investigate tissue characteristics after drying. The area observed was obtained by a cross-sectional cut made in a zone near and parallel to the samples surface and then was coated with a very thin layer of gold under high vacuum conditions before being examined with the microscope. Micrographs were taken at an accelerating voltage of 3 kV, a working distance varying from 1.8 to 3 nm and a magnification of ×300.

Statistical Analysis

All statistical analyses were carried out using the StatGraphics Plus package (StatPoint Technologies, Inc., Warrenton, USA). Results were expressed as mean± standard deviation of the mean (mean±SD). Two-way analysis of variance (ANOVA) was done to establish the presence or absence of significant differences in parameters. Significance level was set at $p<0.05$, and multiple comparisons were performed using the Tukey test (Zar 1999).

Results and Discussion

In this work, a sugar infusion pretreatment and two dehydration methods (air- and freeze drying) were applied to apple disks. After both drying processes, the final water activity of the products ranged between 0.3 and 0.4. Figure 1 shows the water sorption isotherm at 20 °C for freeze-dried (FD) and air-dried (AD) apple disks in a range from 11% to 43% RH. A low RH range was chosen, as these products are developed to be incorporated in low moisture foods. The general behavior showed similar water contents for control and sucrose infusion (SI) freeze-dried samples as well as for control air-dried samples, showing values between ≈5% at 11%RH and 11–14% at 43%RH. A particularly noticeable difference was observed for both SI-AD samples, in which the water content ranged between 1.5% and 3% in the RH range studied. During air drying, movement of water from the interior of the material to its surface causes migration of solutes, and their concentration in outer layers increases, so that they become rigid and often acquire considerable mechanical strength. This phenomenon of crust formation or case hardening is particularly common with foods that contain dissolved sugars and other solutes in high concentration (Potter and Hotchkiss 1995; Rahman and Perera 2007; Ratti 1994). In our case, this phenomenon could be particularly relevant for the SI samples. In additon, sugar impregnation during infusion favors sugar crystallization in the outer layer of the fruit tissue during drying (Rault-Wack 1994). The development of this concentrated solids surface layer (crust), and the reduction in tissue porosity and/or shrinkage due to sugar infiltration and air drying could be responsible for the different water sorption behavior, causing a reduction in water uptake. Thus, the SI-AD samples showed very low water contents along the analyzed RH range.

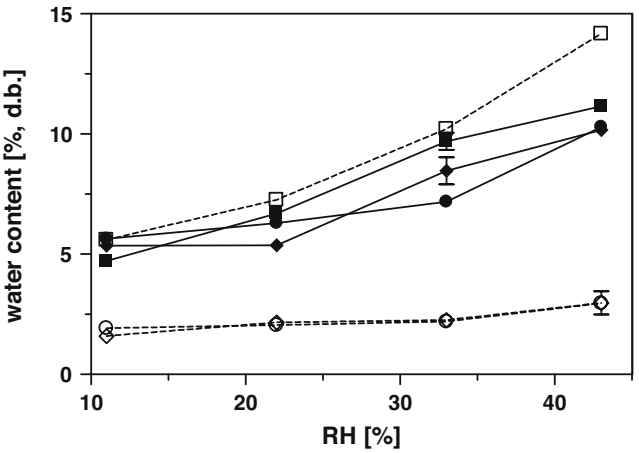

Fig. 1 Water sorption at isotherm at 20 °C for freeze-dried (FD, *solid lines*) and air-dried (AD, *dashed lines*) apple disks subjected to different pretreatments: control-FD (*filled square*), $SI_{0.85}$-FD (*filled diamond*), $SI_{0.92}$-FD (*filled circle*), control-AD (*empty square*), $SI_{0.85}$-AD (*empty diamond*), and $SI_{0.92}$-AD (*empty circle*)

Figure 2 shows typical DSC thermograms showing the glass transition temperature (T_g) for the different apple samples at 22%RH (Fig. 2a) and T_g values as a function of water content (Fig. 2b). All the samples analyzed presented clear glass transitions (Fig. 2a); this was also observed at the other RHs analyzed (not shown). The glass transition temperature values at the analyzed relative humidities were low (ranging from −34 to 7 °C), and all the samples were in the supercooled state at room temperature. Control samples presented relatively similar T_g values for both drying methods. Del Valle et al. (1998), working with air-dried apples (Granny Smith *var.*), obtained T_g values with a difference in the order of 2 °C comparing with our control-AD samples. Our T_g data of control-FD samples are comparable with previous results on freeze-dried apple samples in the same RH range (Acevedo et al. 2006; Sá et al. 1999; Venir et al. 2007), having differences of 7 °C at the most. It has been reported that the T_g of apple samples is coincident with that of apple juice at the same moisture content (Aguilera et al. 1998; Venir et al. 2007). Furthermore, it was shown that the cell wall material does not exhibit a glass transition (Venir et al. 2007).

The SI samples, however, showed a very distinct behavior. The SI-AD samples presented very low T_g values (ranging from −27 to −13 °C), which is not in accordance with the low water content of the samples. This could be related to the crystallization of sucrose caused by the concentration of the sugar upon drying; therefore, crystalline sucrose would not contribute to increase the T_g of the samples, and the available water would plastizice the remaining amorphous phase of the system rendering these very low T_g values. On the other hand, the SI-FD samples presented relatively high T_g values (ranging from −10 to 4 °C); in this case, a proportion of sucrose could be in the amorphous state upon freeze drying, contributing to the increase of the glass transition temperature.

Figure 3 shows the ^{1}H NMR relaxation times (T_2) determined at 25 °C by a single 90° pulse as a function of relative humidity. This fast decay component (T_2) was attributed to solid polysaccharide protons, and water molecules that are strongly associated by hydrogen bonding to the solid matrix (Kalichevsky et al. 1992; Ruan et al. 1999; Rugraff et al. 1996). It can be observed that the samples presented an increase in the T_2 values while increasing RH, and T_2 values varied in a range from 5 to 40 μs. The increase in T_2 can be attributed to the plasticizing effect of water, which provides greater mobility to the solid's protons. Control-FD samples showed higher T_2 values than those observed for control-AD samples (i.e., T_2 values at 43% RH of 24 and 39 μs for control-AD and control-FD samples, respectively), which correlates with

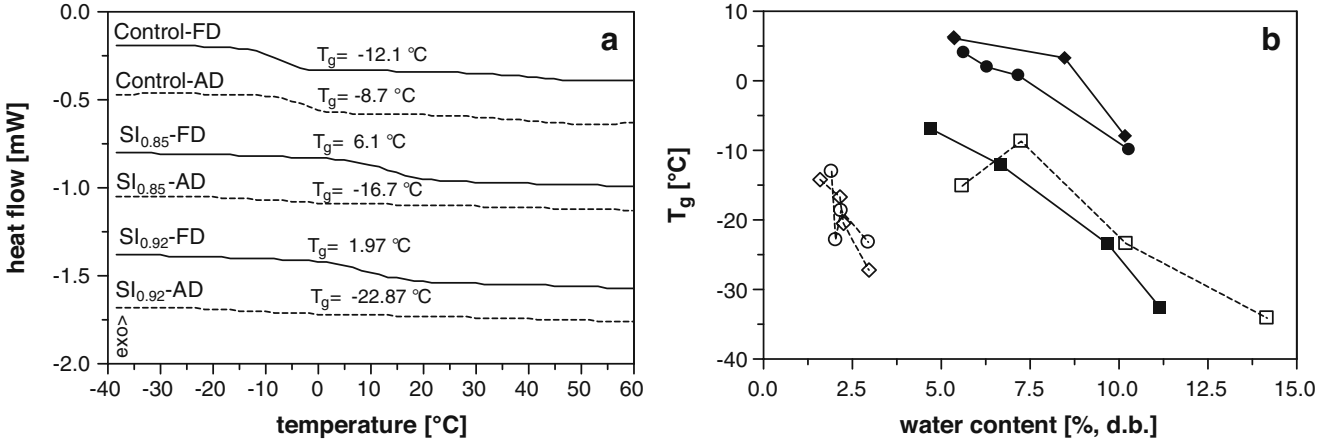

Fig. 2 DSC thermograms for 22%RH samples (**a**) and glass transition temperature (T_g) as a function of water content (**b**) for freeze-dried (FD, *solid lines*) and air-dried (AD, *dashed lines*) apple disks subjected to different pretreatments: control-FD (*filled square*), $SI_{0.85}$-FD (*filled diamond*), $SI_{0.92}$-FD (*filled circle*), control-AD (*empty square*), $SI_{0.85}$-AD (*empty diamond*), and $SI_{0.92}$-AD (*empty circle*)

the slightly higher T_g values observed for these samples (Fig. 2b). The SI-AD samples showed low T_2 values (around 6–9 μs in the range from 11% to 43%RH), and this could be attributed to the low water content at all the RHs analyzed (Fig. 1). On the other hand, the SI-FD samples showed relatively low T_2 values (ranging from 7 and 12 μs), mostly related to the relatively higher T_g values in the RH range studied. No significant differences were observed for the two SI samples analyzed for each drying method. The results presented in Fig. 3 show that the samples pretreated with the sucrose infusion have much lower molecular mobility than the control samples in the RH range analyzed, both for freeze- and air drying. This fact could be an indication that these SI systems could be more stable regarding deteriorative changes.

The parameter firmness or hardness is usually used to evaluate the mechanical properties and is defined as the resistance of a material to deformation or penetration (Szczesniak 1973; Watada 1995). The loss of firmness or crunchiness in dried apples was analyzed through the puncture assay, which simulates the incisors impact at biting (Harker et al. 1996; Roudaut et al. 2002). Mechanical behavior of apple disks subjected to different dehydration processes can be observed in Fig. 4 and Table 1. Force–distance curves obtained during the puncture assay are shown in Fig. 4a–c for freeze-dried samples and Fig. 4d–f for air-dried samples. There was an increase up to a maximum force as the probe was driven into the tissue, and then there was a reduction in the force required to drive the probe further into the fruit following tissue failure. Control-FD apples showed a low resistance to probe penetration with no significant differences ($p<0.05$) between F_{max} values (Fig. 4a, Table 1). The curves shape of these samples indicated their soft behavior, presenting rounded peaks. As the RH increased, the peaks occurred at larger penetration distances, indicating more deformable matrices. Freeze-dried samples previously treated with SI led to different responses according to RH and the amount of infused sugar. At low RH, the force–distance pattern is characterized by several sharp peaks, as occurring in crisp, brittle materials, with F_{max} values greater than those observed for control samples (Fig. 4b, c, Table 1). The increase in RH resulted in smoothing of force–distance curves, and peaks were not observed, which would indicate a loss of crispness. When subjected to air drying, mechanical response in samples without pretreatment (control) exposed to 11% RH (Fig. 4d) was similar to that obtained in freeze-dried control samples at the same RH conditions (Fig. 4a). The mechanical behavior of the FD

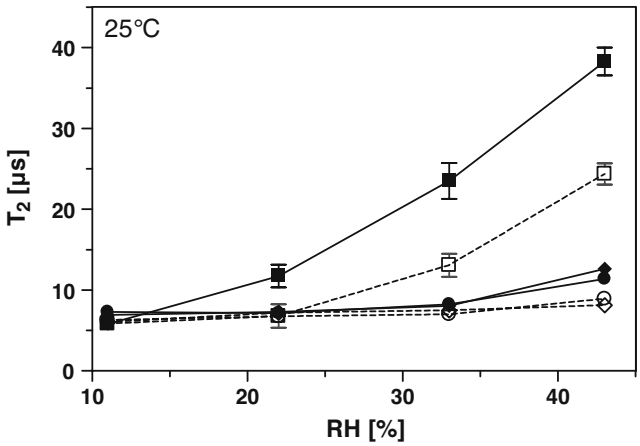

Fig. 3 T_2 relaxation times obtained by ^{1}H NMR as a function of relative humidity for freeze-dried (FD, *solid lines*) and air-dried (AD, *dashed lines*) apple disks subjected to different pretreatments: control-FD (*filled square*), $SI_{0.85}$-FD (*filled diamond*), $SI_{0.92}$-FD (*filled circle*), control-AD (*empty square*), $SI_{0.85}$-AD (*empty diamond*) and $SI_{0.92}$-AD (*empty circle*)

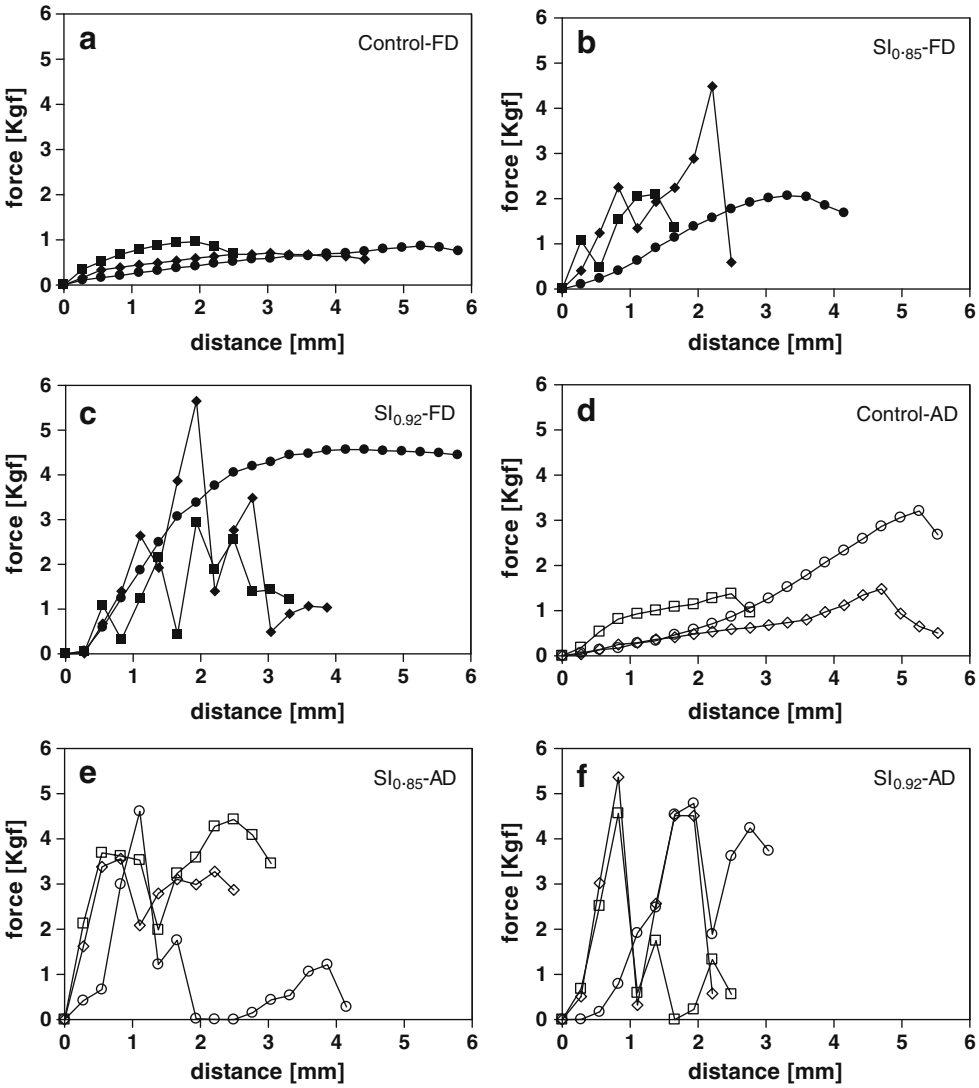

Fig. 4 Force distance curves obtained after puncture assay in freeze-dried (FD, *filled symbols*) samples: control-FD (**a**), $SI_{0.85}$-FD (**b**), and $SI_{0.92}$-FD (**c**), and air-dried (AD, *open symbols*) samples: control-AD (d), $SI_{0.85}$-AD (**e**), and $SI_{0.92}$-AD (**f**). Samples were equilibrated at 11% RH (*filled square*, *empty square*), 22% RH (*filled diamond*, *empty diamond*), and 33% RH (*filled circle*, *empty circle*)

and AD control samples at 22% and 33% RH was very different although the water content was similar (Fig. 1). The AD samples showed a significant increase in F_{max} value, while FD samples showed low F_{max} values. These differences could be due to the structural characteristics caused by the dehydration methods. The effect of water sorption provokes changes in mechanical properties of materials. A dry material may become softer due to the plasticizing effect of water, which leads to a depression of viscosity and a loss of crispy/crunchy behavior. On the

Table 1 Maximum force values (F_{max}) obtained after puncture assays in dehydrated apple disks subjected to different pretreatments as a function of relative humidity

Dehydrated apple disks	RH (%)	Freeze dried		Air dried	
		F_{max}, (kgf)	$SD_{F_{max}}$	F_{max}, kgf	$SD_{F_{max}}$
Control	11	1.02a,A	0.18	1.3a,A	0.4
	22	0.71a,A	0.11	1.4a,B	0.4
	33	0.76[a],A	0.09	2.9bB	1.0
Dry sucrose infusion a_w=0.85	11	2.4b,A	0.7	3.9c,d,A	0.9
	22	4.4c,A	0.6	3.8c,d,A	0.6
	33	1.9b,A	0.7	4.3d,e,B	0.9
Dry sucrose infusion a_w=0.92	11	3.3d,A	0.7	4.5d,e,A	1.2
	22	5.4e,A	0.8	5.4f,A	0.8
	33	4.57c,A	0.17	4.7e,f,A	0.4

$SD_{F_{max}}$ are standard deviations of the means. Single effects were analyzed by Tukey test. Means within rows with a different lowercase letter are significantly different ($p<0.05$). Means within columns with a different uppercase letter are significantly different ($p<0.05$)

other hand, partial plasticization could be accompanied by toughening because moistened structure does not disintegrate so easily (Harris and Peleg 1996; Lewicki et al. 2004). In this case, some humidified samples may exhibit the same or even greater resistance to puncture than completely dried materials. At least in some cereals and snacks, a moderate amount of absorbed moisture causes a simultaneous loss of brittleness and a measurable increase in stiffness or toughness, perceived as hardness by untrained panelists (Peleg 2006). Moreover, the shrinkage that often takes place during air drying causes a significant compactness of structure, and so an increase in hardness. These characteristics of materials after rehydration could explain the increase in F_{max} observed in the air-dried samples equilibrated at 33% RH (Fig. 4d, Table 1). Samples subjected to air drying with previous SI exhibited more irregular force–distance plots, with several sharp peaks over the whole RH range (Fig. 4e, f). According to Peleg (2006), the degree of jaggedness of curves is usually indicative of brittleness. The behavior of SI-AD samples was similar to that obtained in SI-FD samples at low RHs, but exhibited greater maximum forces at high RHs, especially in samples infused till a_w= 0.85. At a_w 0.92 condition, no significant differences were observed between samples at all RHs (Table 1 and Fig. 4b, c, e, f).

Infusion process, as well as the following drying step, affects cells and intercellular space morphology. Usually, in freeze-dried systems, an extensive pore network is left by the sublimation of ice and the presence of intracellular air spaces; therefore, little or no shrinkage takes place. On the contrary, air drying is characterized by extensive shrinkage, which reveals a significant reduction in the number of pores and pore and cell size (Deng and Zhao 2008; Grabowski et al. 2006; Krokida et al. 2001; Rahman 2001; Sagar and Kumar 2010). These differences in tissue behavior upon drying treatments were detected by simple comparison of the tissue structure of products in Fig. 5. SEM micrographs (taken near the sample surface) from control-AD apples (Fig. 5a) showed a larger folding of cells and cell walls, and a full structure more collapsed than that observed in control-FD samples (Fig. 5b), which would explain the greater firmness obtained after air drying. During previous sugar infusion, at least two major simultaneous countercurrent flows take place: an important water flow out of the food into the external medium and a simultaneous transfer of solute from the solution into the food, both occurring due to the water and solute activity gradients across the cell membranes of tissue. Remaining porosity of dried samples could be related to the degree of water loss (WL) and solid gain (SG) during osmosis, to the fruit water content, and to the microstructure changes during drying (osmosis and further dehydration processes). At higher solute concentration of external medium, water loss and sugar gain increase upon sugar infusion, but WL is usually greater than SG (Mandala et al. 2005; Nieto et al. 2004; Reppa et al. 1999). Moreover, it has been shown that penetration of osmoactive substances during osmosis is a surface process, which results in the development of a concentrated surface layer of solids posing an additional resistance to mass transfer and that the magnitude of this phenomenon would be dependent on the degree of cell collapse and sugar incorporation (Salvatori and Alzamora 2000; Salvatori et al. 1998; Azuara et al. 2009). In our case, this effect could be observed for the FD samples with sucrose infusion, in which the maximum forces were lower for the samples infused at a_w 0.85 than those at a_w 0.92 (Table 1). Probably, at a_w 0.85, the sugar penetration was not enough to cover the void spaces and a greater porosity could remain, resulting in a higher tissue softening degree after drying than that observed for the samples at a_w 0.92. At a_w 0.92, a smaller porosity of the material could result from the saturation of intercellular space and cell walls by sugar penetration during previous osmosis. As evidenced by SEM micrographs of Fig. 5d, it was difficult to distinguish between cells and intercellular spaces of freeze-dried apples with previous SI at a_w 0.85, since the layer near the sample surface appeared to be more saturated by sugars when compared to FD samples infused at a_w 0.92 (Fig. 5f). Furthermore, the cell structure could have been more damaged during infusion at a_w 0.85, contributing to the reduction of the resistance to compression of samples after drying. Sugar deposition (marked with letter s) can be clearly appreciated (Fig. 5d and f) and particularly in Fig. 6b, where sugars can be observed in detail located in an intercellular space of tissue in comparison with freeze-dried apples without sugar incorporation (Fig. 6a).

For AD apples, there were no significant differences in hardness among the two SI pretreatments, and the processing resulted in significantly higher hardness values and crispness compared to the AD control samples (Table 1). SEM images confirmed tissue shrinkage in samples infused at both a_w values, as well as the presence of sugars in several zones (Fig. 5c, e). These results indicate that more sugar incorporation previous to air drying affected in the same way the structural characteristics of the matrix at the conditions analyzed in this work.

Infused samples after dehydration rendered higher sucrose contents than control samples: 56% and 38% at a_w 0.85 and a_w 0.92, respectively. These results suggest that it is possible to obtain fruits having variable degrees of sweetness without affecting mechanical response.

Figure 7 shows the variation in L^*, a^*, and b^* parameters observed after the application of pretreatments and drying with respect to a fresh apple sample. The control samples showed higher luminosity values after freeze-drying (L^*=82±2), while control-AD samples showed a

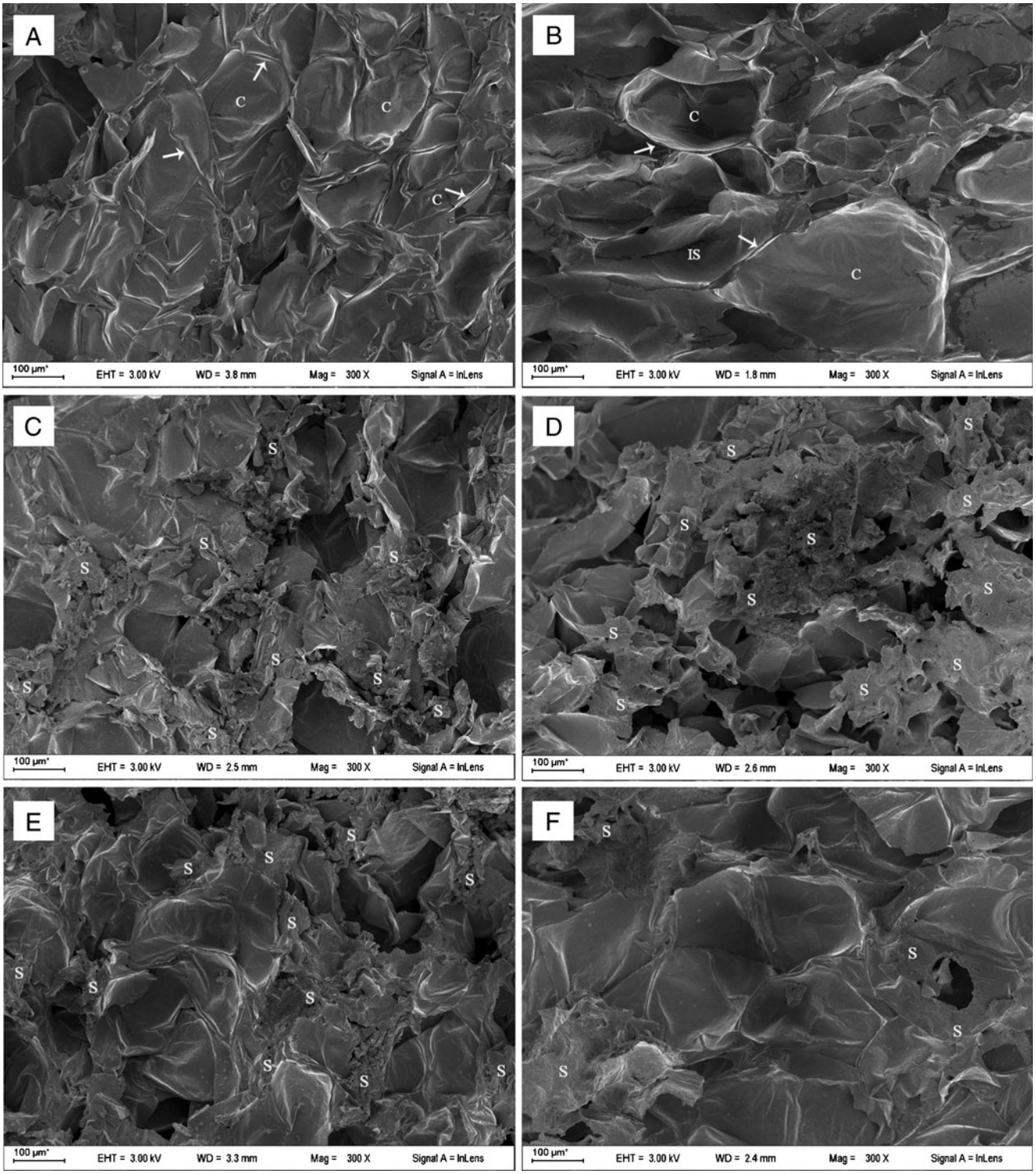

Fig. 5 Scanning electron micrograph of dried apples. **a** Control-AD; **b** control-FD; **c** $SI_{0.85}$-AD; **d** $SI_{0.85}$-F-D; **e**; $SI_{0.92}$-AD; **f** $SI_{0.92}$-F-D. All micrographs were taken near the samples surface. *S* sugar, *C* cell, *IS* intercellular space. *Arrows* indicate tissue cell walls

decrease in the L^* parameter ($L^*=73\pm1$), mainly due to browning development (Fig. 7a). All the SI pretreated samples showed similar L^* values (L^* between 78 and 80), which were slightly higher than those for the fresh samples ($L^*=78\pm2$). The addition of sulfites to the dried mixture prepared for SI, which could prevent browning reactions, and the sugar crust formed on the apple disk surface, which would provide a whiter appearance, could be responsible for the increase in L^* values compared to the control-AD samples. Regarding the color variables, the FD method

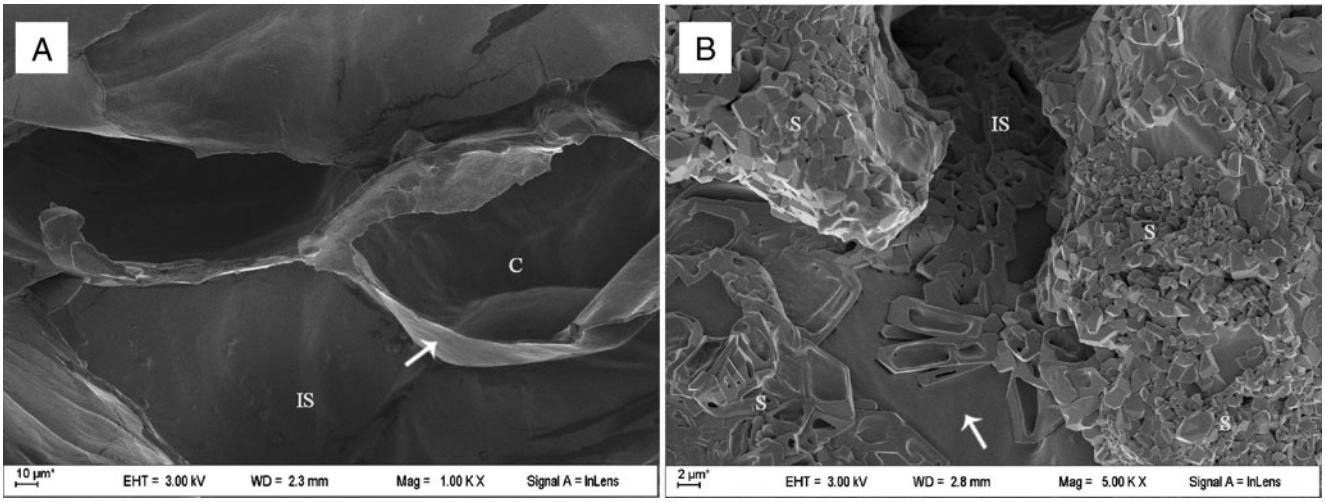

Fig. 6 Scanning electron micrograph of dried apples at high magnification. **a** Control-FD; **b** $SI_{0.85}$-FD. The micrographs were taken near the samples surface. *S* sugar, *IS* intercellular space. *Arrows* indicate tissue cell walls

allowed to retain a^* values more similar to those of the fresh sample (Fig. 7b). The control-AD samples showed a shift from green to red and an important increase in the b^* value ($b^*=22\pm2$; Fig. 7b, c). Both changes, together with the decrease in L^* (Fig. 7a), could be associated to browning development. All the SI samples presented an increase in a^* values (however, they remained similar to the fresh sample) and also an important increase in the b^* values (Fig. 7b–c). Mandala et al. (2005) showed that browning was considerably hindered when a sugar impregnation was used as pretreatment of apples before drying at 55 °C, giving a final product close to that of a fresh fruit. The infusion of sugars in fruits caused a relative stability of the L^*, a^*, and b^* color parameters for air-dried apples and bananas that otherwise experienced extensive browning (Krokida et al. 2001). Freeze-drying inhibited color deterioration of several fruits and vegetables during drying, resulting in products with superior color compared to those dried by other methods (Krokida et al. 2001). The color variables were also determined after humidification, although no significant changes were observed (data not shown).

The combination of drying methods with sugar pretreatments led to matrices bearing different characteristics when compared with those obtained with drying alone. An advantage of sugar infusion as a pretreatment is that it provided dehydrated materials with lower water contents than those for the control samples in the analyzed RH range. Since these materials adsorbed less water, lower T_2 values were obtained, which implies a lower molecular mobility of solids and of water associated to them. In addition, infusion conditions were of great consequence on the final mechanical properties of dried apples. The fruits obtained were harder and crispier than the control samples, even under unfavorable conditions of relative humidity.

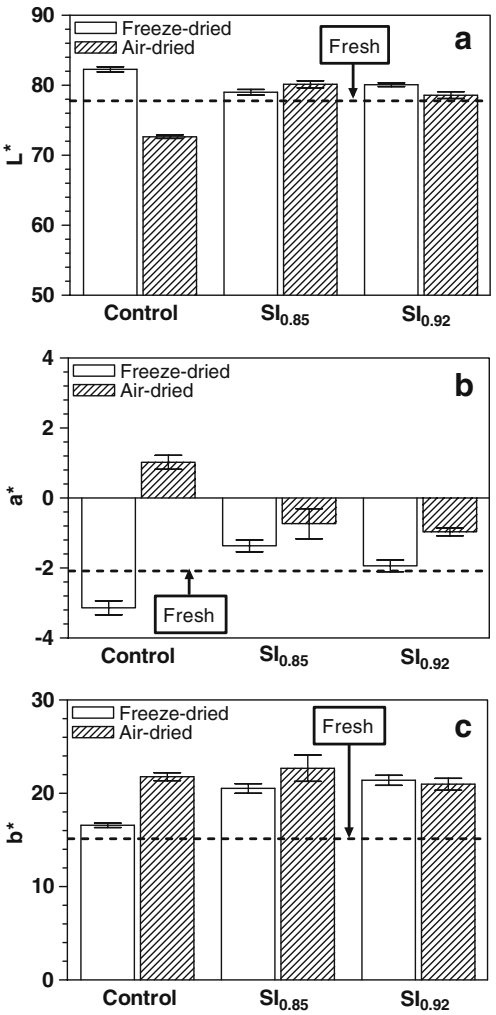

Fig. 7 Color values (L^*, a^*, and b^*) obtained after drying compared to the fresh sample

These results do not agree with the obtained T_g values, as all the samples were in the supercooled state at room temperature. T_g has been considered an indicator of food stability, as it is a function of the amount of residual water acting as a plasticizer and mobility enhancer in dried materials. However, in the case of dried fruits, the relationship between T_g and some stability features such as textural properties might not be clear. T_g is a characteristic of the water soluble phases, and the mechanical behavior in dried fruits is mainly dependent on other phases (non-soluble compounds of the cell matrix) and on other phenomena, such as porosity, the process of shrinkage, and case hardening, which can play an important role in explaining texture in some instances when glass concept is not valid.

Regarding color, although there were some changes, particularly in the chromatic variables, the general aspect of the samples was good. Sensory tests should be performed in order to assess the acceptability of this type of products.

Conclusions

Overall, the results of this work suggest that upon sucrose infusion pretreatment and dehydration procedures, high quality (regarding color and texture) stable products (regarding water content and molecular mobility) can be obtained. Furthermore, the different sucrose proportions in the infusion allow obtaining products with different sweetness degree, which might be considered for various applications without affecting in a great manner the quality and stability analyzed factors. Sucrose infusion also contributed to lower molecular mobility of solids as assessed by NMR. This aspect could contribute to reduce the impact of deteriorative changes along storage.

The results obtained are useful in the selection of the suitable processing technology of dried apple fruits of high quality for direct consume or for the incorporation to compound foods and also in determining storage conditions at which undesirable changes in color and texture are avoided. FD samples offered materials bearing better color quality (the color of the samples was closer to that of the fresh apple) and also with more porous structure. Therefore, this drying method could be more appropriate to generate products that could be easily rehydrated (for confectionary, desserts, etc.). In the case of air-dried samples, the crispy texture could be kept up to higher RH than FD samples, which could be an advantage to incorporate these products as ingredients into certain foods such cereal bars or fruit chips.

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