Vol. 15, No. 2 (2016) 441-456
Revista Mexicana de Ingeniería Química

STRUCTURAL PROPERTIES CHANGES DURING OSMOTIC DRYING OF PLANTAIN (*Musa paradisiaca* AAB) AND ITS ROLE ON MASS TRANSFER

CAMBIOS EN LAS PROPIEDADES ESTRUCTURALES DURANTE EL SECADO OSMÓTICO DE PLANTAIN (*Musa paradisiaca* AAB) Y SU ROL EN EL TRANSPORTE DE MASA

I. Gallegos-Marin[1], L.L. Méndez-Lagunas[1]*, J. Rodríguez-Ramírez[1], C.E. Martínez-Sánchez[2]
[1]*Instituto Politécnico Nacional, CIIDIR Oaxaca, Hornos 1003, Santa Cruz Xoxocotlán, Oaxaca, 71230, México.*
[2]*Departamento de Ingeniería Química y Bioquímica, Coordinación de Posgrado e Investigación, Instituto Tecnológico de Tuxtepec, Calz. Dr. Víctor Bravo Ahuja s/n, Col. 5 de Mayo, Tuxtepec, Oax, CP 68350, México.*
Received March 11, 2016; Accepted May 14, 2016

Abstract
This work studies the structural properties of plantain (*Musa paradisiaca* AAB) during osmotic dehydration (OD) and its role on mass transfer phenomena. Drying temperatures of 40, 60 and 80°C and sucrose solutions of 29 and 45°Brix were used in OD. Apparent and true volume, were measured using volumetric displacement and gas stereopycnometer methods. Apparent (ρ_b) and true densities (ρ_p) were calculated with volume data. Porosity (ε) and shrinkage (S) were calculated based on ρ_b and ρ_p data. Apparent diffusion coefficient (D_{aw}) of water and solids (D_{as}) were calculated. Micrographs were obtained for both, raw and dehydrated samples. The major water loss (WL) was found at 45°Brix dehydrated at 40 and 60°C, whereas the major solid gain (SG) was obtained at 45°Brix dehydrated at 80°C. A non-linear volume dependence on loss moisture, as well as a ρ_p and ρ_b increase and ε reduction with two pseudo-equilibrium periods was found. Micrographs at different depths of the food tissue revealed the effect treatments on two structural anisotropy areas. Shrinkage, starch gelatinization and swelling, as well as anisotropy affect the mass transfer.
Keywords: plantain, osmotic dehydration, structural properties, mass transfer.

Resumen
Este trabajo estudia las propiedades estructurales de plátano (*Musa paradisiaca* AAB) durante el secado osmótico (OD) y su rol en el fenómeno de transferencia de masa. Temperaturas de secado de 40, 60 y 80°C y soluciones de sacarosa de 29 y 45°Brix fueron usadas en OD. Volumen aparente y real fueron medidos usando el método de desplazamiento volumétrico y estereopicnómetro de gas. Densidad aparente (ρ_b) y real (ρ_p) fueron calculados con los datos de volumen. Porosidad (ε) y encogimiento (S) fueron calculados en base a los datos de ρ_b y ρ_p. El coeficiente de difusividad aparente (D_{aw}) de agua y sólidos (D_{as}) fue calculado. Micrografías fueron obtenidas de muestras frescas y deshidratadas. La mayor pérdida de agua (WL) fue encontrada a 45°Brix deshidratadas a 40 y 60°C, mientras que la mayor ganancia de solidos (SG) fue obtenida a 45°Brix deshidratada a 80°C. Una dependencia no lineal de la perdida de humedad, incremento de ρ_p y ρ_b y reducción de ε con dos periodos de seudoequilibrio, fueron encontrados. Micrografías a diferentes profundidades del tejido del alimento revelo el efecto del pretratamiento en dos estructuras anisotrópicas. El encogimiento, gelatinización de almidón e hinchamiento, así como la anisotropía afectan la transferencia de masa.
Palabras clave: plantain, deshidratación osmótica, propiedades estructurales, transferencia de masa.

1 Introduction

Osmotic dehydration (OD) is frequently used as a pre-treatment in several processes in order to obtain intermediate moisture food with shelf-life enhanced features, or as a pre-treatment to reduce energy consumption and/or heat damage in other traditional dehydration processes (Tregunno *et al.*1996; Monsalve *et al.* 1993).

Osmotic dehydration is a common process of water removal that is applied to food material and consists in place food tissue, such as fruits and vegetables, in a hypertonic solution. Between the solution and the food there is a significant pressure

* *Corresponding author. E-mail:* mendezll@hotmail.com

difference, providing the driving force to remove water, while the cellular membrane works as a semi-permeable membrane. Water diffusion takes place together with a simultaneous counter diffusion of the osmotic-solution solutes within the tissue. The membrane that is responsible for the osmotic transport is not perfectly selective and other solutes within cells can also be lixiviates in the osmotic solution (Giangiacomo *et al*. 1987). When a fruit or vegetable is submitted to a dehydration process produces changes in the chemical, physical and structural characteristics of the plantain tissue, such as changes in volume, porosity, changes in mechanical properties and color changes (Lozano *et al*. 1983; Mayor and Sereno 2004; Telis *et al*. 2005; Krokida *et al*. 2000).

Such properties are related to the control and improvement of quality and unit operations process design (Perera, 2005; Roa *et al*. 2005). Fluxes of heat and mass transfer during dehydration processes modify the chemical composition, as well as the physicochemical and mechanical properties of the material (McLauhglin *et al*. 1998; Lewicki and Lukaszuk 2000). For example, porosity has been associated with the chemical stability of dry products, sugar degradation and lipid oxidation.

During OD some authors have found a non-linear correlation, between volume and moisture content, which seems to depend on the viscoelastic properties of the tissues and structural changes (e.g. cell wall alteration, middle lamella division, membrane lysis, tissue shrinkage, etc.). Other authors, instead, detected a strong linear relationship between shrinkage and volume changes (Barat *et al*. 1998; Lazarides and Mavroudis 1996; Alzamora *et al*. 2000; Nieto *et al*. 1998; Torreggiani and Bertolo 2004; Raghavan and Silveira 2001).

Several mechanisms have been proposed to explain mass transfer during OD:

1. Those depending on concentration gradients, mainly effective or apparent diffusion (D_{eff}) o pseudo-diffusion (PDM), which can usually be modeled with the solution of Fick's equation (Barat *et al*., 2001).

2. Those affected by pressure gradients, mainly hydrodynamic mechanisms (HDM). These occur at ambient pressure when cells get linearly deformed with water loss and the gas-phase volume in intercellular spaces increases, leading to pressure gradients in the tissue (Barat *et al*. 2001).

3. Those promoted by the cell structure of the material. Mass transfer is carried out by three transport means: apoplasmic transport (outside cell membranes) or movement of the material within the cellular volume, the symplasmic transport (within the plasma membrane), defined as the material transport among close cells through the plasmodesmata and the transmembrane flux. Recently a new transportation means has been described as fluid phase endocytosis (Chiralt and Fito 2003).

Effective diffusion (D_{eff}) is a macro-component related to a homogeneous microstructural level and implies irreversible thermodynamics. D_{eff} is a proportionality coefficient associated with the concentration gradient, which cannot completely explain mass transfer during osmosis. Another type of strengths such as osmotic pressure (concentration gradient) and permeability (internal capillary pressure) are not considered in this mechanism (Torreggiani and Bertolo 2004; Gekas, 2001; Shi and Le 2002; Ferrando and Spiess 2001).

According to the HDM approach, the cellular structure surface collapses in case of a volume reduction of the internal pore when the osmotic solution concentration and/or temperature are high. This probably causes a partial expulsion of the osmotic solution due to the internal gas release when pores shrink.

Within the framework of the mechanisms explained according to their gradients of activity and pressure (CPG), volume changes can be justified by the internal pressure in intracellular spaces. Since the OD process accelerates the impregnation of the pore, it follows different steps.

At the beginning of the process, capillary pressure increases the external liquid gain, whereas the internal gas of pores is compressed and thus flows outwards. Later in the process, an irreversible partial loss of gas takes place and residual gas will be compressed again, increasing the capillary liquid gain. When water loss (WL) taken place, cells shrink and intracellular volume increases, making a larger volume available for the gas phase, reducing internal pressure and promoting the external liquid suction. The mechanical equilibrium in the pore will be reestablished with the subsequent penetration of the liquid according to the current radius of pores. This process will be ongoing until pores are completely impregnated.

Due to the complexity of phenomena taking place during OD, in addition to solution properties and

process conditions, other variables shall be considered in order to explain mass transfer mechanisms, among which cellular properties, initial and material structure (D_{eff}, tortuosity and porosity), modification in composition and structural changes (shrinkage, porosity reduction, cell collapse).

Tissue changes significantly affect cellular compartmentalization, intracellular volume, and matrix wall and membrane. These changes greatly affects transport properties and modify the heat and mass transfer. In addition, heat and mass transfer behavior of the product are modified (Torreggiani and Bertolo 2004).

Furthermore, material plant tissue is not always uniform. Substantially different dehydration and solute-uptake rates have been found in different raw material undergoing the same OD treatment (Torreggiani and Bertolo 2004).

Plantain tissue, composed by endocarp and exocarp, shows a structural anisotropy, which may affect its micro-structural properties and mass transfer behavior.

This work aims at assessing the development of structural (Vp, ρ_b, ρ_p, ε, Sb) and microstructural properties, as well as of water and solid apparent diffusion (D_a during the plantain OD and at matching such properties with the mass transfer mechanisms proposed in the literature.

2 Materials and methods

2.1 Material preparation

The material used was plantains at a flowering time between 2.0 to 2.5 months after the first hand appeared. Green plantains in ripening phase 2 (Gallegos *et al*. 2013) (pale green, sugar content 13.6 g/kg, solids soluble content 1.3°Brix, pulp firmness 4.22 kgf) were acquired by a local producer (18°04'52" N, 96°07'07 W). The material was cleaned, peeled and cut in slices 1.6 ± 0.6 mm thick and diameter was of 3.2 ± 0.03 cm.

2.2 Osmotic dehydration

Samples were soaked in sucrose osmotic solutions (OS) of 29 and 45°Brix kept at a constant temperature of 40, 60 and 80ºC, respectively, under constant stirring (120 rpm) in a hot plate stirrer (Thermo Scientific Cimarec USA). In order to maintain a constant concentration of sucrose in the osmotic solution and prevent significant changes during the dehydration process, an osmotic solution/sample ratio of 15:1 w/w was applied.

Water loss and solid gain were determined by taking samples at various time intervals; during the first 15 minutes samples were taken every 3 minutes and then at 45, 105, 165, 225, 285 minutes. For all treatments 3 replicates were performed. Surface water was eliminated with absorbent paper.

2.3 Determination of moisture content

Moisture content was determined by drying a sample for 24 hours at 110°C. The results were expressed as percentage of wet basis (AOAC 1980).

2.4 Osmotic dehydration kinetics

The osmotic process was study using water loss (WL) and solid gain (SG) equations. Eqs. 1 and 2 were applied to calculate WL and SG.

$$WL(\%) = \left(\frac{w_i X_i - w_f X_f}{w_i}\right) \times 100 \tag{1}$$

$$SG(\%) = \left(\frac{w_f X_{sf} - w_i X_{si}}{w_i}\right) \times 100 \tag{2}$$

2.5 Determining the apparent diffusion coefficient of water and solids

The equation for mass transfer by diffusion in unsteady-state has frequently been employed to describe both water loss and solids gain during the OD process.

Assuming that diffusion is in one direction, the process is isothermal and the solution Fick's second law for diffusion in terms of rectangular coordinates for infinitely long flat plates according to (Crank, 1979) it is:

$$\frac{C_t - C_e}{C_i - C_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2}{4} \frac{D_{eff} t}{l^2} \right) \right] \tag{3}$$

Where C indicates water loss or concentration of solids in the product.

In order to calculate diffusion coefficients the slope method was used. The approach was to consider from time zero until the equilibrium point of moisture content and total solids of each treatment.

2.6 *True density (ρ_p)*

A stereopycnometer, (model SPY - 5DC Quantachrome, Boynton Beach, Florida USA) was used at a pressure of 1.1951 kg /cm^2 ± 0.003. The equipment calibration was carried out with a standardized steel sphere. In order to determine volume, a sample of 15 ± 2 g was used. From the data obtained in the stereopycnometer, the true volume was calculated with Eq. (4).

$$V_p = V_c + \frac{V_A}{1 - \frac{P_1}{P_2}} \tag{4}$$

The true density was adjusted to the moisture content of the sample and determined with Eq. (5).

$$\rho_p = \frac{w_1}{V_1} = \frac{w - w_2}{V_p - \frac{w_2}{\rho_2}} \tag{5}$$

2.7 *Apparent density (ρ_b)*

ρ_b was determined by using a non-covered sample of 1.5 ± 0.25 g with the volume-displacement method and it was calculated according to Eq. (6). The sample was soaked in hexane and the measurement was carried out with a density kit (Sartorius YDK 01-OD, Goettingen, Germany) in < 10 s in order to prevent the immersion-liquid absorption.

$$\rho_b = \frac{w_{s-a}\rho_{ii}}{w_{s-li}} \tag{6}$$

2.8 *Porosity (ε)*

It was calculated according to Kassama and Ngadi (2004) with Eq. (7).

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} \tag{7}$$

2.9 *Shrinkage*

The shrinkage may be determined by considering initial volume (V_i) as a reference with the following equation (Madiouli *et al*. 2007).

$$S = \frac{V_i - V}{V_i} \times 100 \tag{8}$$

2.10 *Preparation of sections for microscopic examination*

Tests with optical microscope (LM) (Olympus CX31, Center Valley, USA) and FEI Quanta 3D FEG environmental scanning electron microscope (ESEM) were carried out in cuttings of surface tissues and transversal ones at different depths (100 and 800 μm) of fresh and OD-treated samples. Fresh samples with a cutting of 40-μm depth were observed in LM. The criterion followed to select the time when micrographs were taken was according to equilibrium point of solids, only for treated samples.

In fresh samples endocarp and mesocarp of fresh and processed samples were determined the average length starch granules and pore diameter. The pore diameter was determined by comparison of scales, using ESEM images and Infinity Analyze (Lumenera Corporation) software. The average pore diameter of the granules observed in the image is reported.

2.11 *Statistical analysis*

A 2 x 3 completely-random factorial experiment was used to assess the effect of temperature and sucrose concentration on water loss, solid gain, ρ_b, ρ_p and ε. Data were compared with an analysis of variance (ANOVA) and Tukey's method (P<0.05) was followed to determine pair differences with the statistical software Minitab for Windows (Minitab, Inc., State College, PA, USA).

3 Results and discussion

Fig. 1 and 2 show the effect of temperature and OS concentration on water loss (WL) and solid gain (SG). The lowest WL was found at process conditions of 29°Brix and 80°C, whereas the highest WL level at 45°Brix and 60°C. Statistically drying temperature showed no significant differences (P< 0.05) on WL at the end of the drying, while a significant effect of temperature and OS concentration on the SG and WL respectively, was found.

As process temperature and OS increased, SG did as well. At both OS concentration and 80ºC, water mass transfer is quicker compared with other process temperatures. WL stability was reached at 45 min (80°C), 160 min (60°C) and 220 min (40°C) for both OS concentrations, whereas SG became stable at 300 min for all process conditions.

Similar results have been reported by Singh *et al*. (2007) for carrot OD, Torreggiani (1993) in fruits and vegetables, Nowakunda *et al*. (2004) and Porciuncula *et al*. (2013) in banana slices, who found relevant WL effect during the first 2 hours and remove of water up to 60% water removal during the first hour. OS

effect on WL is consistent with the one found by Heng *et al*. (1990); Bolín *et al*. (1983); Alakali *et al*. (2006) during OD of papaya, melon, potato and banana, respectively, using sucrose solutions as a hypertonic medium. Kaymak-Ertekin and Sultanoglu (2006) and Telis *et al*. (2005) reported similar SG due to the effect temperature had on the kinetics of apple and meat OD.

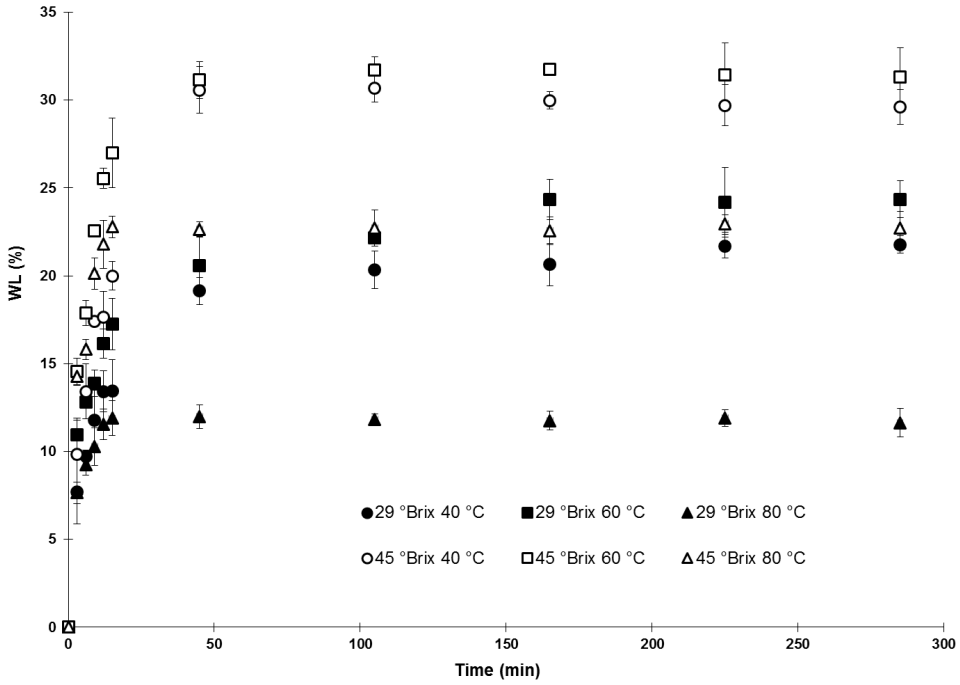

Fig. 1. Water loss (WL) during OD.

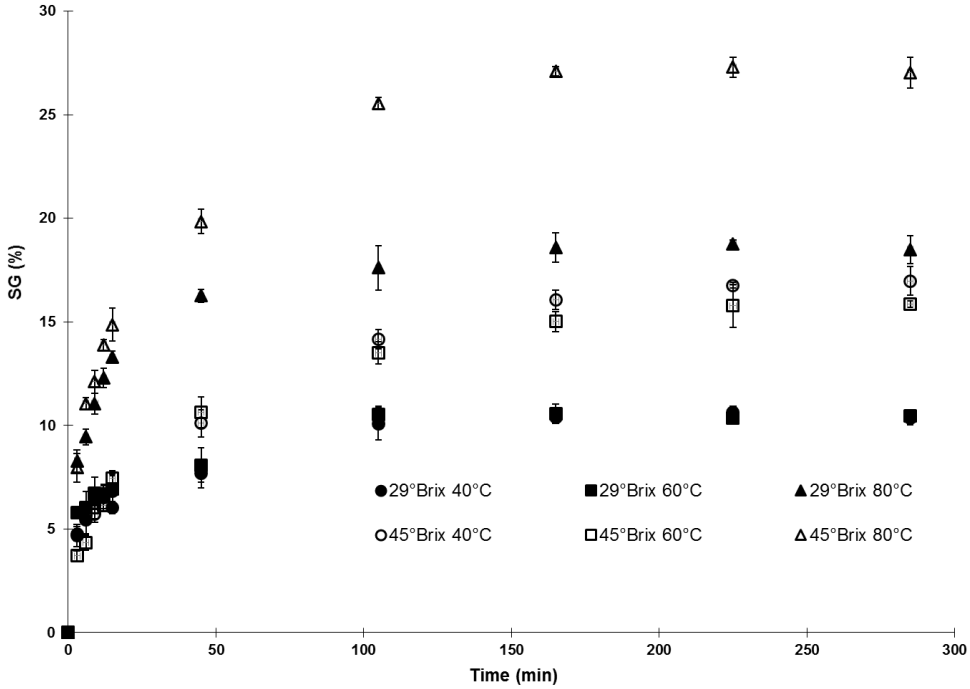

Fig. 2. Solid gain (SG) during OD.

Table 1 Water and solids diffusion coefficients during OD

Treatments	D_{aw} ($m^2/s \times 10^{-10}$)	D_{as} ($m^2/s \times 10^{-10}$)
29%, 40°C	1.50 ± 0.12^{D}	0.81 ± 0.39^{B}
29%, 60°C	1.16 ± 0.71^{D}	0.86 ± 0.21^{B}
29%, 80°C	7.80 ± 3.0^{A}	1.44 ± 0.89^{B}
45%, 40°C	3.3 ± 1.18^{C}	3.5 ± 1.0^{A}
45%, 60°C	3.74 ± 2.7^{C}	3.72 ± 2.4^{A}
45%, 80°C	5.6 ± 3.7^{B}	3.86 ± 0.82^{A}

$^{A-B}$Values with the same letter in the same column are not significantly different (P <0.05)

WL is lower than 80°C because at this temperature occur starch swelling of plantain. Starch granules untreated are insoluble in cold water and have a highly organized structure, however, when these are heated, begins a slow water absorption process in the zones intermicellar (amorphous), which are less organized and more accessible. As the temperature increases, more water is retained and the starch granules swells and increases in volume, forming a paste or gel which prevents water loss.

Starch swelling in inter-mycelium amorphous areas, which are less organized due to water absorption, reduces water outlet, in addition a barrier which prevented the flow of water is formed.

WL, SG and apparent diffusion coefficients (D_{aw} and D_{as}) increase with temperature and concentration (Table 1), confirming the effect on mobility of water molecules and osmotic gradient. Nevertheless, during OD, variations in WL and SG suggest that other phenomena intervene in the process before the equilibrium is reached.

The order of magnitude of D_{eff} for water (D_{aw}) and solids (D_{as}) is very similar (Table 1), contradicting the molecular diffusion theory. Taken into account the significantly different size of solute and water molecules (2.75 and 9 Å, respectively), the mass transfer of these molecules should be different as well. Furthermore, the molecular diffusion is related to the D_a in the concepts of tortuosity and pore diameter of the solid material being diffused.

A minimum difference of D_{aw} and D_{as} have been reported in numerous publications for large numbers of foods, however, D_{aw} should be higher transfer solutes, thus, the diffusion-mechanism applicability to explain the solute mass-transfer in solids is apparently accidental (Treybal *et al.* 1980).

Consequently, it is to be expected that moisture distribution within solids at the different drying stages will not be similar to the diffusion mechanism. If considering that solute transfer mainly takes place on the surface of solids as "impregnation", then the adsorption mechanisms and surface diffusion may explain the solute mass transfer in solids during the osmotic drying.

A different behavior for the high temperature conditions seems to appear at a macroscopic level in correspondence with starch gelatinization.

Several studies have showed that gelatinization temperature (Tp) of starches isolated from fruits depends on the moisture content, temperature, water activity (Aw), and ripening stage of granules and, in sugar solutions, also on the size of sugar molecules.

According to Beleia *et al.* (1996), above 30% moisture, Tp of starches remains constant and it was confirmed that the presence of sugar solutions increases the onset temperature of starch gelatinization.

Gelatinization onset temperatures in starches isolated from plantains and bananas at different ripening stages were reported in the range 74-81.5°C, whereas Tp was reported in the range 74.0-80.7°C (Beleia *et al.* 1996; Lii *et al.* 1982). The average moisture content of the sample was 58.9% (w.b), while the average final one was 38.5% (w.b.). Consequently, it is to be expected that Aw will remain in a relatively-high range and Tp will remain lower than 81°C during OD.

The formation of a paste is most favored when used the drying temperature of 80°C. At such temperature, an amylose and amylopectin paste was formed, which may explain how quickly stability was reached. Process temperatures lower than 60ºC show a significant reduction of water and solids? transfer, which can be explained with a swelling phenomenon. Both swelling and gelatinization were confirmed when assessing physical properties and SEM images.

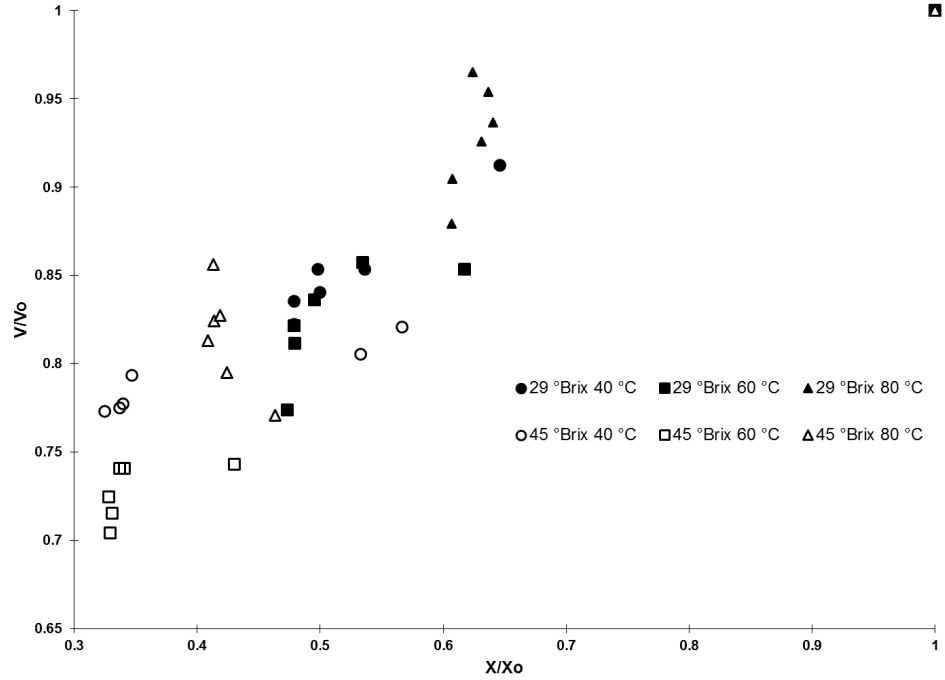

Fig. 3. Changes of volume (V/Vo) during OD.

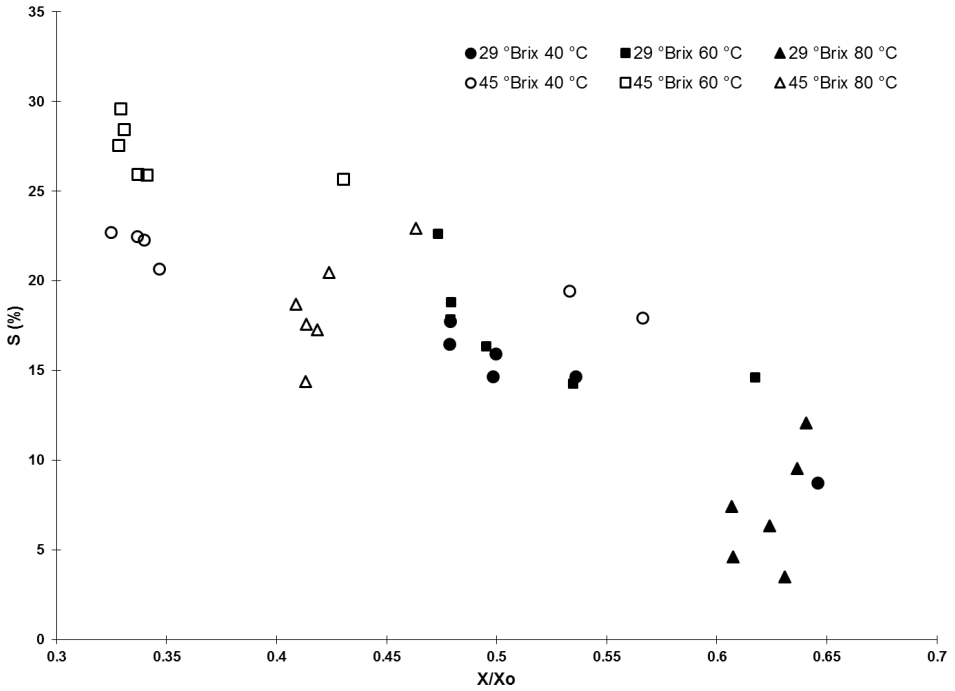

Fig. 4. Shrinkage (S) during OD.

3.1 Physical properties

3.1.1 Volume change and shrinkage

Fig. 3 shows volume changes during OD. For the process temperatures of 40 and 60°C in both OS concentrations, a linear volume relation with moisture content was found up to X>0.64, followed by a asymptotic period and ending with volume decrease. For treatments at 80°C, instead, a volume increase was found, ending with a constant volume reduction without noticing any changes in moisture content. In none of the treatments volume was recovered similarly to the initial amount.

Volume change due to water reduction in materials undergoing drying has been widely used to explain lineal relation. Moreover, non-lineal relation with moisture content was explained according to the theory of internal pressure in intercellular spaces, intercellular membrane saturation due to the impregnation of solids, swelling of inter-mycelium areas and deformation-relaxation phenomena of cell wall matrix (Barat *et al*. 1998; Nuñez-Santiago *et al*. 2004). Chiralt and Fito (2003) instead, proposed the hydrodynamic flux theory to explain volume recovery.

Shrinkage (S), shown in Fig. 4, increases with OS concentration and is independent from moisture content when OS temperature is higher than Tp of starches. A constant increase in moisture content is detected when OS temperature is lower than starches' Tp. S variations are consistent with changes resulting from gelatinization of starches, leading to colloidal dispersion, whereas the osmotic gradient lead S to increase.

3.1.2 True density anhydrous, apparent density and porosity

In order to assess whether internal pressure in intercellular spaces increase liquid or solid gain at the beginning of the process, true density (ρ_p) anhydrous and apparent density (ρ_b) were measured. True density anhydrous is defined as the quotient of mass over the volume of a sample, without considering pores. ρ_b is defined as the relationship between the mass and volume of the material, including pores (Rodríguez-Ramírez *et al*. 2012).

ρ_p kinetic are shown in (Fig. 5). In the first 15 minutes, ρ_p increases in all treatments, consistently with solids gaining velocity (Fig. 6). Such results suggest that at the beginning of the process the content of the densest substances (sucrose) increases in the sample. During this period an important effect of temperature and OS concentration on velocity gain of solids was found. Strong process conditions (80°C, 45°Brix and 29°Brix) affect the permeability of the structure of the material and facilitate the inlet of solutes while promoting mass transfer. Between 50 and 150 min, ρ_p remains constant, before undergoing a period of increases and decreases. In mild conditions at the final stage, ρ_p, increases compared to the initial ρ_p, while in strong conditions it drops significantly. Mild conditions favor the swelling of starch granules and makes membranes more permeable, which promotes mass transfer. In strong conditions, instead, gelatinization is favored, which blocks mass transfer.

An exponential behavior of ρ_b depending on the time was found (Fig. 7). A significant effect (α=0.05) of temperature and OS concentration on ρ_b was detected. Some process conditions (29°Brix) showed little increases and decreases of ρ_b.

ρ_b upward exponential behavior suggests an increase in solids and volume of the gas phase of the pores. Similar trends have been reported by Mayor *et al*. (2011) in pumpkin OD and by Nieto *et al*. (1998) in apple OD. During OD of different fruits, ρ_b showed ascending, descending and fluctuating stages (Lozano *et al*. 1983; Krokida and Marouli 1997), the latter of which can be explained by the physicochemical properties, chemical composition, initial porosity or anisotropic physical structure of the material affecting the stress degree during the process (Rahman, 2001; Flores *et al*. 2013).

When the process is about to reach the chemical equilibrium, both ρ_b and ρ_p show an increase related to the cell-wall mechanical relaxation (Chiralt and Fito 2003). Relaxation of mechanical stress producing volume and mass recovery was observed in different levels depending on the plant tissue (Fito *et al*. 2001). When materials are heated up, they can either expand or contract leading to volume variations. ρ_p and ρ_b variations suggest an expansion and contraction of membranes during OD that may vary the internal pressure in intracellular spaces.

Porosity (ε) behavior during OD is shown in fig. 8. A decrease in the first 50 min followed by two equilibration periods -the first one between 50 and 200 min and the second between 200 and 300 min was found. A significant ε loss was experienced in high-temperature process conditions.

This behavior, with ε fluctuating periods, is consistent with the ones reported in different fruits (Lozano *et al*. 1983; Krokida and Maroulis 1997; Mavroudis *et al*. 1998; Giraldo *et al*. 2003).

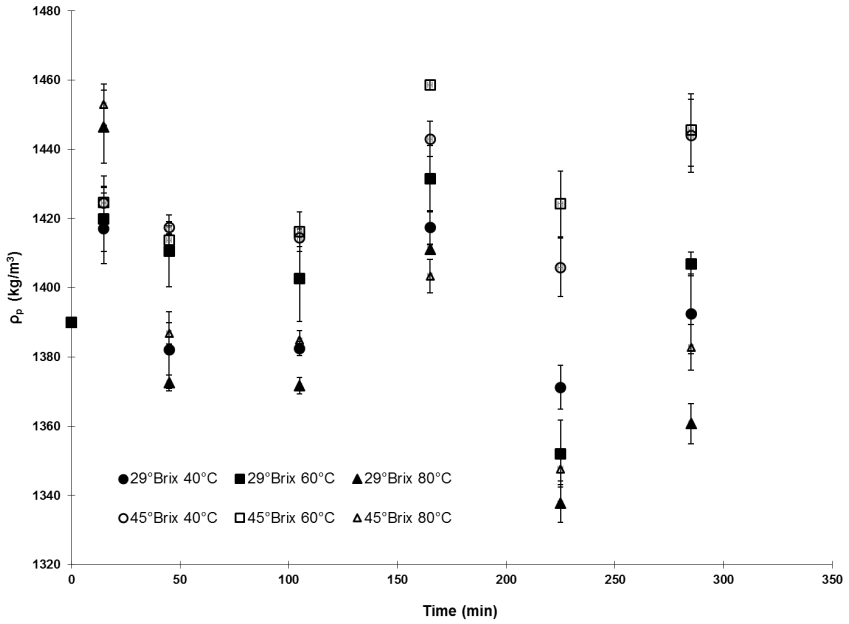

Fig. 5. Changes in true density (ρ_p) during OD

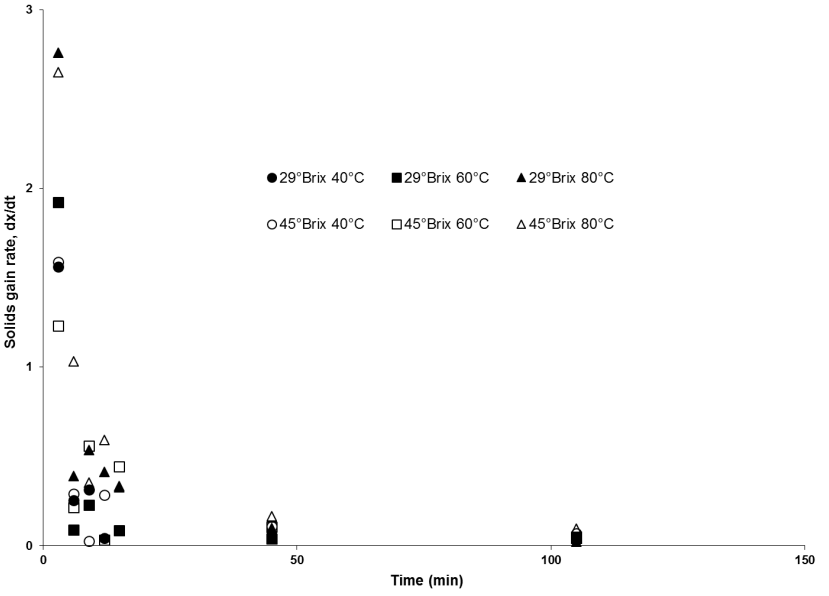

Fig. 6 Solid gain rate during OD.

It has been suggested that porosity initial reduction is due to the quick initial impregnation of the tissue with the osmotic solution, penetrating within external pores for capillary forces and sucrose accumulation in the external surface of the material. The latter forms a thick layer hindering the additional penetration of the osmotic solution, while also minimizing the gas flow from the material to the solution. However, this theory could not be confirmed in the micrographs, which showed no barrier sucrose. Moreover, results confirm the HDM theory suggesting the volume reduction of the internal pore. Even if the volume of pores was not calculated in this work, ε indicates a fraction of holes in the material, which decreases while OD progresses.

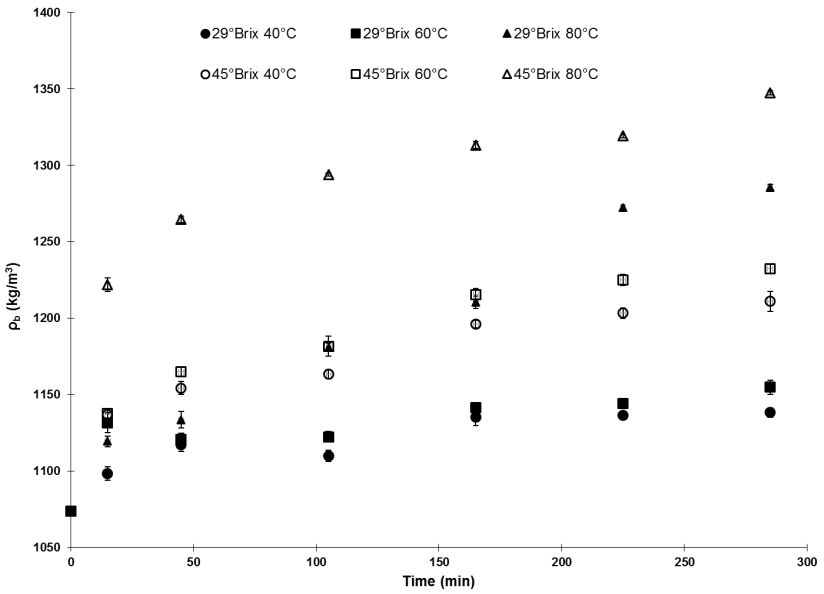

Fig. 7. Changes in apparent density (ρ_b) during OD.

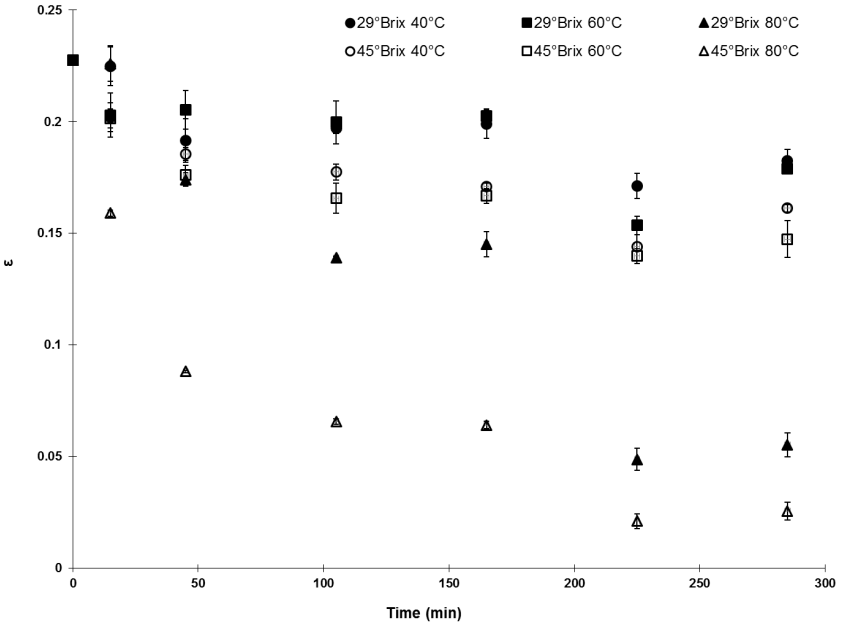

Fig. 8. Changes in porosity (ε) during OD

Chiralt and Fito (2003) propose that the mechanisms responsible for mass transport depend on plant tissue structure and process time. Several proposed mechanisms are observed at different levels: whole tissue, internal porous structure and cell walls and membranes (Aguilera *et al*. 1999).

3.2 Analysis of the microstructure of plantain

According to Tee *et al*. (2011) plantain structure has three locus in the pulp area: Internal walls' locus are rich in parenchyma and starch. In the ripening phase 2, the size of parenchyma cells increases and within

these cells, starches can be found.

At a macroscopic level, two clearly-distinguishable regions can be observed: endocarp - central parts where seeds are to be found- constituting approximately 50% and exocarp - the most external part.

Cuttings at a 40 mm depth in fresh-banana exocarp samples observed with LM show starch granules with a regular oval shape and a smooth and well-formed surface (Fig. 9a) The structures observed in Figure 9 are similar to those reported in Rivas-González *et al*. (2004), Hernández-Jaimes *et al*. (2013), de la Rosa-Millan (2014) and Jane *et al*. (1994) in banana and plantain. Samples treated at 45°Brix of sucrose, instead, show the deformation of starch granules at low temperatures and swelling at high temperatures of process (Fig. 9b and 9c). The average dimensions of starch and pores are displayed in table 2.

ESEM micrographs of exocarp and endocarp surfaces are shown in (Fig. 10). The endocarp presented a great quantity of pores, with a larger diameter than in the exocarp. The size of granules is larger in the exocarp than in the endocarp (Table 2).

The surfaces of samples treated at low temperature (Fig. 11a and 12a) present non-well-defined starch granules, as well as cell lysis and a reduction in the characteristic length of granules.

In Fig. 11b no starch granule can be observed, but rather the presence of a paste caused by the starch lixiviation and a reduction in the number of pores. In fig. 11c the very few granules that can be noticed experienced a swelling and there is also a paste of gelatinized starch.

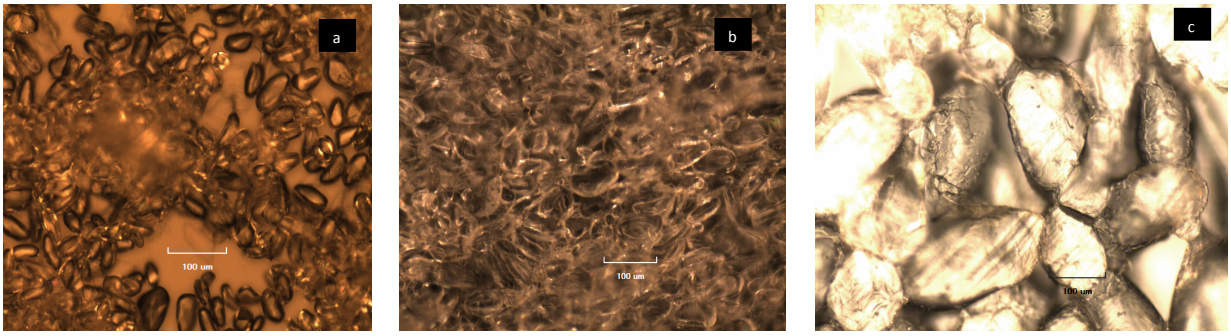

Fig. 9 LM micrographs of plantain exocarp, magnification 40X. (a) untreated, (b) treated to 45 °Brix 40 °C, (c) treated to 45 °Brix 80 °C.

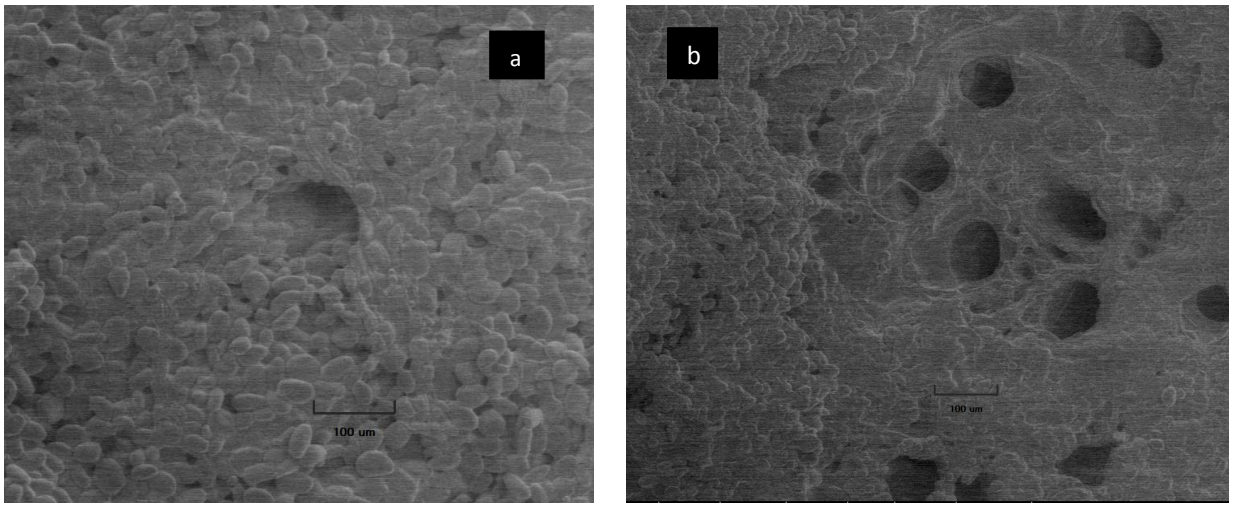

Fig. 10. ESEM micrographs from surface of untreated plantain, 200X magnification. (a) exocarp (b) endocarp.

Table 2. Average diameter of plantain structures observed in ESEM.

Treatment	Section	Average length starch granules (μm)	Pore diameter (μm)
Untrated	Endocarp	25.83 ± 5.8	81-125
Untreated	Exocarp	50.5 ± 9.3	20.5 ± 6.9
29°Brix 40°C	Exocarp	23.18 ± 3.9	20.61 ± 6.38
29°Brix 80°C	Exocarp	NO	20.4 ± 12.81
45°Brix 40°C	Exocarp	52.6 ± 8.0	17.5 ± 4.2
45°Brix 80°C	Exocarp	98.79 ± 37.4	22-66

NO Not observed

Table 3. Average pore diameter at different depths of cut plantain observed in ESEM

Treatment	Section	Depth of cut (μm)	Pore diameter (μm)
29°Brix 40°C	Exocarp	100	43.29 ± 4.4
29°Brix 40°C	Exocarp	800	39.98 ± 5.28
29°Brix 80°C	Exocarp	100	20.54 ± 5.1
29°Brix 80°C	Exocarp	800	24.77 ± 4.1
45°Brix 40°C	Exocarp	100	16.98 ± 1.08
45°Brix 40°C	Exocarp	800	19.23 ± 2.18
45°Brix 80°C	Exocarp	100	18.22 ± 3.1
45°Brix 80°C	Exocarp	800	19.05 ± 4.1

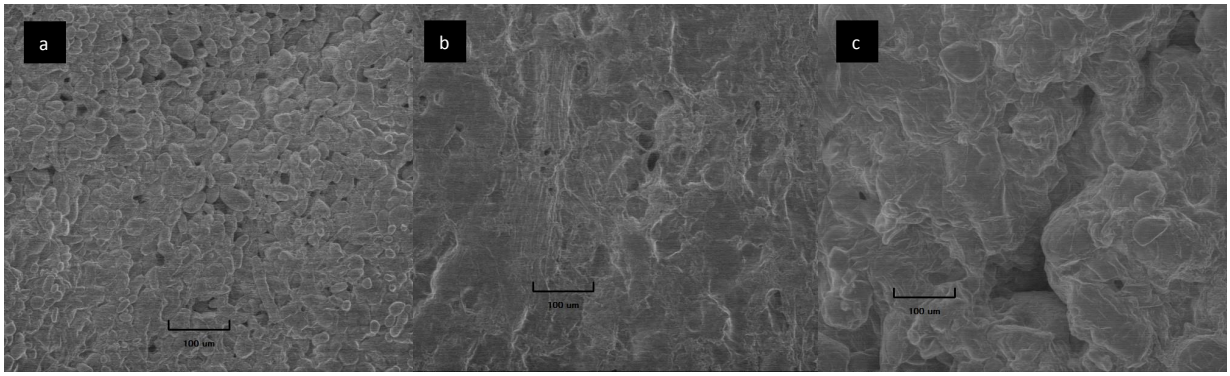

Fig. 11 ESEM micrographs from surface of exocarp plantain, 200X magnification. (a) treated to 29 °Brix 40°C (b) treated to 29°Brix 80°C (c) treated to 45°Brix 80°C.

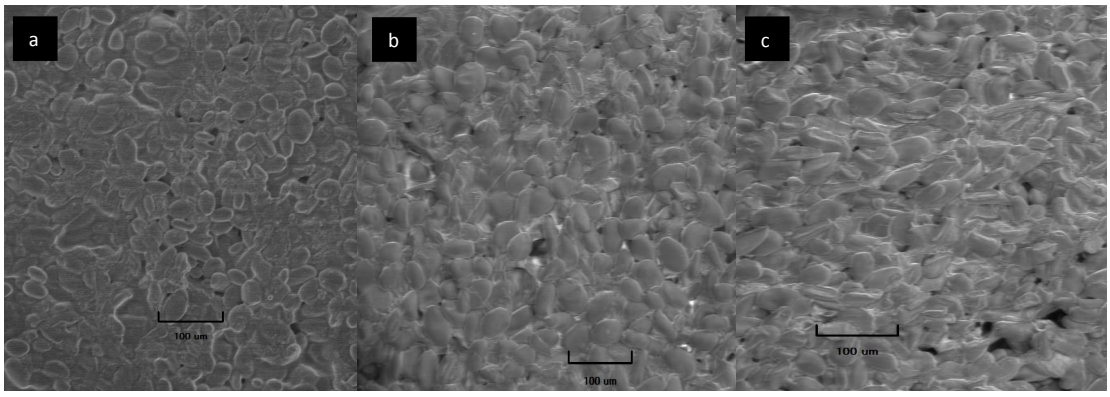

Fig. 12 ESEM micrographs from exocarp treated to 45 °Brix 40 °C, 200X magnification. (a) surface (b) cut to 100 μm in depth (c). cut to 800 μm in depth.

OS concentration affects the structure: as a matter of fact, a lower concentration was accompanied by a reduction of the average length of starch granules at low temperatures, whereas at high temperatures a complete lysis of starch granules was experienced and no definite granule was detected on the surface (Table 2).

The pore size at different depths of cut is presented in Table 3. A effect of concentration on the pore size was observed at 29 ° Brix where larger pores in the tissue subjected to 45 ° Brix found. These results are explained because there was a greater concentration of solids higher gain, which means that there was greater impregnating solid. Moreover, larger pores at a depth (800 μm) were found, suggesting that the mass transfer of solids would be a surface phenomenon.

Images show the effect of temperature, since at 80ºC a swelling and starch gelatinization, as well as pore obstruction were observed (11b and 11c). The diameter of pores not significantly decreases compared to the fresh variant. Samples exposed to a higher temperature experienced a more significant deformation and gelatinization.

Cuttings of samples at a depth of 100 and 800 μm showed a relevant shrinkage, which increases according to the level of depth (Fig. 12). The diameter of pores is larger in deeper layers due to the shrinkage leaving spaces or holes. The opposite process is observed in surface layers where swelling close pores.

Rastogi *et al*. (2000) suggest three water-transfer levels during osmotic treatment of potatoes: water diffusion in front of the intact core of material to the transition layer, water diffusion at the transition layer, and water diffusion through a layer where cells have been damaged by osmotic stress.

According to Torreggiani and Bertolo (2004) structural differences may explain the quantitative different behavior. The significant porosity reduction in strong conditions is due to the swelling of granules and the formation of a mass or gel to extract amylose and amylopectin. The swelling observed in surface layers may be due to the osmotic liquid maintaining starch granules hydrated. In internal layers, instead, granules ended their mass transfer process, favoring volume recovery in treatments at 80ºC.

The anisotropy of the material hinders the explanation of mass transfer mechanisms during the OD process. Anisotropy may also explain the lack of linearity between volume and water loss, as well as the observed changes in ρ_b during drying process.

Conclusions

Structural changes during OD suggest that at cellular level the following phenomena are experienced: the expansion and contraction of membranes, ρ_b increase, ε reduction and S increase shows changes in the diameter of pores.

ESEM images of materials under temperature conditions that are higher or lower than Tp indicate that at various depth levels in the material different phenomena are registered: on the surface there is starch swelling or gelatinization, whereas inside there are different shrinkage levels. In these images, no thick barrier of high-molecular-weight solutes that may block mass transfer is observed. The increase or decreases of pores due to the changes of starches are deeply related to water and solids diffusion coefficients. Shrinkage is strongly related to the physical and chemical changes of starches due to OD treatments, although these changes are observed at the micro level, they are not reflected in the characteristic length (l) value of D_{eff} equation. The pore size found at greater depths are larger, which suggesting that the mass transfer of solids would be a surface phenomenon.

The solution of Fick's second law equation assumes that mass transfer is performed in a continuum medium. An isotropic medium has direction-independent physical and chemical properties. In OD the changes of the material are multidimensional at macro- and microscopic level. The lack of material uniformity makes it difficult to explain the transfer mechanism and diffusion of solutes does not explain completely the-mass transfer phenomenon during OD. In addition, the values of diffusion coefficients of solids have the same order of magnitude water have. Nevertheless, such values should be very different due to the size of molecules being diffused, then other mechanisms such as impregnation should be considered to explain the mechanisms of mass transport.

Acknowledgments

The authors wish to thank the Instituto Politécnico Nacional-Mexico for the financial support provides through the SIP Project: 20130767, CONACyT (grant 237890), BEIFI-IPN and COFFA-IPN. The authors thank PhD Mayahuel Ortega Avilés and Claudia Ramos Torres from Centro de Nanociencias, Micro y Nanotecnologías (CNMN-IPN) for his assistance in Optical and SEM images.

Nomenclature

WL	Water Loss (%)
SG	Solid Gain (%)
w	mass of the sample (g)
Xw	moisture content (gw/(gw+gs+gdm) where w=water, s=solute, dm=drier matter
Xs	solute concentration, in osmotic drying (gs/(gw+gs+gdm)
t	time
e	equilibrium
V	volume (m^3)
V_A	aggregate volume of gas, He, P=0.050 kg cm^{-2} (m^3)
P	pressure (Pa)
ρ	density (kg m^{-3})
ε	porosity
S	shrinkage (%)
w_1, w_2	mass of anhydrous plantain and mass of water contained in plantain (g)
V_1, V_p	volume of anhydrous plantain and total volume of plantain (water + anhydrous plantain) (m^3)
Subscripts	
i	initial
f	final
si	solid initial
sf	solid final
p	true
b	apparent
c	volume of cell container of simple
1	before VA
2	after de VA
w	water
li	liquid immersion
s-a	sample in air
s-li	sample in liquid immersion

References

Aguilera, J.M., Stanley, D.W. (1999). *Microstructural Principles of Food processing and Engineering*. Aspen Publisher Inc. Gaithersburg Maryland USA.

Alakali, J.S., Ariahu, C.C., Nkpa, N.N. (2006). Kinetics of osmotic dehydration of mango. *Journal of Food Processing and Preservation 30*, 597-607.

Alzamora, S.M., Castro, M.A., Vidales, S.L., Nieto, A.B., Salvatori, D. (2000). In: Alzamora, S.M., Tapia, M.S., López-Malo, A. (ed). *Minimally Processed Fruits and Vegetables Fundamental Aspects and Applications*. Aspen Publishers, Inc. Gaithersburg, MD USA

AOAC. (1980). *Official Methods of Analysis* (13th ed.). Association of Official Analytical Chemists, Washington, DC.

Barat, J.M., Chiralt, A., Fito, P. (1998). Equilibrium in cellular food osmotic solution systems as related to structure. *Journal of Food Science 63*, 836-840.

Barat, J.M., Fito, P., Chiralt, A. (2001). Modeling of simultaneous mass transfer and structural changes in fruit tissues. *Journal of Food Engineering 49*, 77-85.

Beleia, A., Miller, R.A., Hoseney, R.C. (1996). Starch gelatinization in sugar solutions. *Starch?Stärke 48*, 259-262.

Bolin, H.R., Huxsoll, C.C., Jackson, R. (1983). Effect of osmotic agents and concentration on fruit quality. *Journal of Food Science 48*, 202-205.

Chiralt, A., Fito, P. (2003). Transport mechanisms in osmotic dehydration: the role of the structure. *Food Science and Technology International 9*, 179-186.

Crank, J. (1979). *The Mathematics of Diffusion*. Oxford University Press, Ely House, London.

de la Rosa-Millan J., Agama-Acevedo E., Osorio-Díaz P. (2014). Efecto del cocimiento, anillado y almacenamiento en la digestibilidad y las características fisicoquímicas de harina de plátano verde. *Revista Mexicana de Ingeniería Química 13*, 151-163.

Doulia, D., Tzia, K., Gekas, V. (2000). A knowledge base for the apparent mass diffusion coefficient (DEFF) of foods. *International Journal of Food Properties 3*, 1-14.

Ferrando, M., Spiess, W. (2001). Cellular response of plant tissue during the osmotic treatment with sucrose, maltose, and trehalose solutions. *Journal of Food Engineering 49*, 115-127.

Fito, P., Chiralt, A., Betoret, N., Gras, M., Cháfer, M., Martínez-Monzó, J., Andres, A., Vidal, D. (2001). Vacuum impregnation and osmotic

dehydration in matrix engineering: Application in functional fresh food development. *Journal of Food Engineering 49*, 175-183.

Flores-Andrade E., Pascual-Pineda L.A., Jimenez M., Beristain C.I. (2013). Effect of whey protein-sucrose in the osmotic dehydration of apple. *Revista Mexicana de Ingeniería Química 12*, 415-424.

Gallegos, M.I., Méndez, L.L., Rodríguez, R.J., Martínez, S.C.E., Muñiz, B.S. (2013). Cambios químicos durante la maduración de platano macho (*Musa paradisiaca* AAB), *XII Conferencia internacional Sobre Ciencia y Tecnología de los Alimentos*. Cuba.

Gekas, V. (2001). Mass transfer modeling. *Journal of Food Engineering 49*, 97-102.

Giangiacomo, R., Torreggiani, D., Abbo, E. (1987). Osmotic Dehydration of Fruit: Part 1. Sugars Exchange between Fruit and Extracting Syrups. *Journal of Food Processing and Preservation 11*, 183-195.

Giraldo, G., Talens, P., Fito, P., Chiralt, A. (2003). Influence of sucrose solution concentration on kinetics and yield during osmotic dehydration of mango. *Journal of Food Engineering 58*, 33-43.

Heng, K., Guilbert, S., Cuq, J.L. (1990). Osmotic dehydration of papaya: influence of process variables on the product quality. *Sciences des Aliments 10*, 831-848.

Hernández-Jaimes, C., Bello-Perez, L. A., Vernon-Carter, E. J., Alvarez-Ramirez, J. (2013). Plantain starch granules morphology, crystallinity, structure transition, and size evolution upon acid hydrolysis. *Carbohydrate Polymers 95*, 207-213.

Jane, J. L., Kasemsuwan, T., Leas, S., Zobel, H., Robyt, J. F. (1994). Anthology of starch granule morphology by scanning electron microscopy. *Starch-Stärke 46*, 121-129.

Kassama, L. S., Ngadi, M. O. (2004). Pore development in chicken meat during deep-fat frying. *LWT-Food Science and Technology 37*, 841-847.

Kaymak-Ertekin, F., Sultanoğlu, M. (2006). Modelling of mass transfer during osmotic dehydration of apples. *Journal of Food Engineering 46*, 243-250.

Krokida, M.K., Karathanos, V.T., Maroulis, Z.B. (2000). Effect of osmotic dehydration on color and sorption characteristics of apple and banana. *Drying Technology: An International Journal 18*, 937-950.

Krokida, M.K., Maroulis, Z.B. (1997). Effect of drying method on shrinkage and porosity. *Drying Technology: An International Journal 15*, 2441-2458.

Lazarides, H.N., Mavroudis, N.E. (1996). Kinetics of osmotic dehydration of a highly shrinking vegetable tissue in a salt-free medium. *Journal of Food Engineering 30*, 61-74.

Lewicki, P.P., Lukaszuk, A. (2000). Effect of osmotic dewatering on rheological properties of apple subjected to convective drying. *Journal of Food Engineering 45*, 119-126.

Lii, C.Y., Chang, S.M., Young, Y.L. (1982). Investigation of the physical and chemical properties of banana starches. *Journal of Food Science 47*, 1493-1497.

Lozano, J.E., Rotstein, E., Urbicain, M.J. (1983). Shrinkage, porosity and bulk density of foodstuffs at changing moisture contents. *Journal of Food Science 48*, 1497-1502.

Madiouli, J., Lecomte, D., Nganya, T., Chavez, S., Sghaier, J., Sammouda, H. (2007). A method for determination of porosity change from shrinkage curves of deformable materials. *Drying Technology: An International Journal 25*, 621-628.

Mavroudis, N.E., Gekas, V., Sjöholm, I. (1998). Osmotic dehydration of apples. Shrinkage phenomena and the significance of initial structure on mass transfer rates. *Journal of Food Engineering 38*, 101-123.

Mayor, L., Moreira, R., Sereno, A.M. (2011). Shrinkage, density, porosity and shape changes during dehydration of pumpkin (*Cucurbita pepo* L.) fruits. *Journal of Food Engineering 103*, 29-37.

Mayor. L., Sereno, A.M. (2004). Modelling shrinkage during convective drying of food materials: a review. *Journal of Food Engineering 61*, 373-386.

McLaughlin, C.P., Magee, T.R.A. (1998). The determination of sorption isotherm and the isosteric heats of sorption for potatoes. *Journal of Food Engineering 35*, 267-280.

Monsalve-Gonzalez, A., Barbosa-Cánovas, G.V., Cavalieri, R.P., Mcevily, A.J., Iyengar, R. (1993). Control of browning during storage of apple slices preserved by combined methods. 4?Hexylresorcinol as anti-browning agent. *Journal of Food Science 58*, 797-800.

Nieto, A., Salvatori, D., Castro, M.A., Alzamora, S.M. (1998). Air drying behavior of apples as affected by blanching and glucose impregnation. *Journal of Food Engineering 36*, 63-79.

Nowakunda, K., Andrés, A., Fito, P. (2004). Osmotic dehydration of banana slices as a pre-treatment for drying process. In: *Proceedings of the 14th International Drying Symposium*, São Paulo, Brazil, 2004.

Núñez-Santiago, M.C., Bello-Pérez, L.A., Tecante, A. (2004). Swelling-solubility characteristics, granule size distribution and rheological behavior of banana (*Musa paradisiaca*) starch. *Carbohydrate Polymers 56*, 65-75.

Perera, C.O. (2005). Selected quality attributes of dried foods. *Drying Technology: An International Journal 23*, 717-7.

Porciuncula, B.D., Zotarelli, M.F., Carciofi, B.A., Laurindo, J.B. (2013). Determining the effective diffusion coefficient of water in banana (Prata variety) during osmotic dehydration and its use in predictive models. *Journal of Food Engineering 119*, 490-496.

Raghavan, G.S.V., Silveira, A.M. (2001). Shrinkage characteristics of strawberries osmotically dehydrated in combination with microwave drying. *Drying Technology: An International Journal 19*, 405-414.

Rahman, M.S. Toward prediction of porosity in foods during drying: a brief review (2001). *Drying Technology: An International Journal 19*, 1-13.

Rao, MA., Rizvi, S.H., Datta., A.K. (2005). *Properties of Food* (ed) Taylor and Francis Group: Boca Raton, USA.

Rastogi, N.K., Angersbach, A., Knorr. D. (2000). Evaluation of mass transfer mechanisms during osmotic treatment of plant materials. *Journal of Food Science 65*, 1016-1019.

Rivas-González M., Zamudio-Flores P. B., Bello-Pérez L. A. (2009). Efecto del grado de acetilación en las características morfológicas y fisicoquímicas del almidón de plátano. *Revista Mexicana de Ingeniería Química 8*, 291-297

Rodríguez-Ramírez, J., Méndez-Lagunas, L., López-Ortiz, A., Sandoval-Torres, S. (2012). True density and apparent density during the drying process for vegetables and fruits: a review. *Journal of Food Science 77*, R146-R154.

Shi, J., Le, M. (2002). Osmotic dehydration of foods: mass transfer and modeling aspects. *Food Reviews International 18*, 305-335.

Singh, B., Kumar, A., Gupta, A.K. (2007). Study of mass transfer kinetics and effective diffusivity during osmotic dehydration of carrot cubes. *Journal of Food Engineering 79*, 471-480.

Souraki, B. A., Ghavami, M., Tondro, H. (2014). Correction of moisture and sucrose effective diffusivities for shrinkage during osmotic dehydration of apple in sucrose solution. *Food and Bioproducts Processing 92*, 1-8.

Tee, Y.K., Ding, P., Rahman, N.A.A. (2011). Physical and cellular structure changes of Rastali banana (*Musa* AAB) during growth and development. *Scientia Horticulturae*, 382-389.

Telis, VRN., Telis-Romero, J., Gabas, A.L. (2005). Solids rheology for dehydrated food and biological materials. *Drying Technology: An International Journal 23*, 759-780.

Torreggiani, D. (1993). Osmotic dehydration in fruit and vegetable processing. *Food Research International 26*, 59-68.

Torreggiani, D., Bertolo, G. (2004). Present and future in process control and optimization of osmotic dehydration. *Advances in Food and Nutrition Research 48*, 173-238.

Tregunno, N.B., Goff, H.D. (1996). Osmodehydrofreezing of apples: structural and textural effects. *Food Research International 29*, 471-479.

Treybal, R.E., Rodríguez, A.G., Lozano, F.J. (1980). *Mass Transfer Operation*. McGraw-Hill, New York.