Recent advances on the understanding of the *nixtamalization* process

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In this work we study the effect of the *nixtamalization* time on the structural, morphological and thermal properties of the corn pericarp. We also studied the semi-quantitative changes in the chemical composition of the pericarp by x-ray diffraction. By correlating the results obtained by x-ray diffraction and photoacustics we propose that *nixtamalization* can be viewed as a series of physicochemical phenomena that involve hemicellulose dissolution, swelling, alkaline cellulose formation and phase transition between native and mercerized cellulose. We found consistent values for some physical properties of the raw pericarp.

Keywords: *nixtamalization*, corn pericarp, x-ray diffraction, microscopy, photoacustics.
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1.Introduction

Corn has been the feed base of Mesoamerican peoples from the ancient times. In Mexico, corn is used as the main raw material to make *tortillas*, among other food products. By a traditional method, called *nixtamalization*, the corn is cooked in a solution of water with lime to be lately milled after an overnight steeping, to obtain a wet dough (*masa*) from which *tortillas* are formed. However, corn processing has currently adopted two main tendencies: substituting the traditional method in making *tortilla*s, because of the economic and technological benefits of instantaneous corn flour; and a significant growth in the consumption of packaged *tortilla*. Additionally, the increased popularity of Mexican food in the United States had generated an additional demand for *tortillas* and corn flour.[1-3] However, the organoleptic requirements are high and hence Mexican still prefer the traditionally prepared *tortilla*; moreover, the *nixtamalization* process itself and the physicochemical changes that take place in the corn during their processing are not fully understood although several works had been published that study the influence of several factors on the *tortilla*,[4-6] the flour/dough[7-9] and on the pericarp properties.[10-13] It has been suggested that the quality of the processed corn flour is determined by the quantity of pericarp incorporated,[10-11] giving to the *tortilla* flexibility, and mechanical and thermal resistance, as well as a particular taste. In fact, it has been pointed out that only the pericarp might be *nixtamalized*, while the endosperm only has to be ground and incorporated into the flour.[14] Nevertheless, to the best of our knowledge there is not a study dedicated to the changes that pericarp suffers during the processing time. In this work we study the changes that take place in the corn pericarp during a typical nixtamalization process, by combining x-ray diffraction, photoacustics and scanning electron and atomic force microscopies.

2. Experimental Details

Maicena type corn has been used. Traditional *nixtamalization* with 100 g corn, 300 ml water and 2 g $Ca(OH)_2$ was performed at 85±5 °C by 30 min. After cooking, corn was allowed to overnight steep. Samples were taken at different times of the process (t_r). Once obtained, they were rinsed, dehydrated and peeled to obtain the pericarp. X-ray diffraction (XRD) measurements were performed in a Siemens D5000 with Cu k_α radiation using the grazing incidence geometry. Atomic force microscopy (AFM) was performed in a Autoprobe CP in the contact mode. Scanning electron microscopy (SEM) was performed in a Jeol JSM 35C on previously Al-coated pericarps. Photoacustics (PA) was performed with a mechanically modulated Ar-laser in the open cell geometry. From XRD we calculated the crystallinity and chemical composition and from PA, the thermal diffusivity of the samples. The morphological changes were observed from 800 x 800 μm^2 to 5 x 5 μm^2 by combining SEM and AFM.

3. Results and Discussion

X-ray diffraction semi-quantitative analysis

Due to its semicrystalline nature, pericarp diffractograms show wide peaks and low intensities, so it could be difficult to obtain valuable information from them. However, by using a multigaussian deconvolution as in Fig. 1, we obtained the present components in the crystalline fraction of the diffractogram, that corresponds

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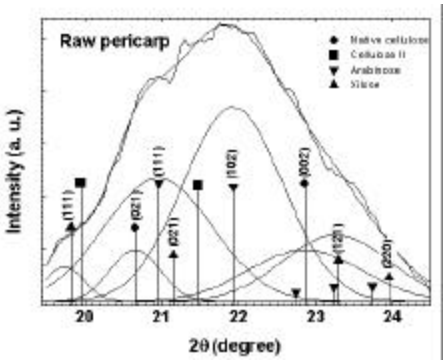

Fig. 1 Deconvoluted x-ray diffractogram of raw corn pericarp.

to the crystalline areas in the pericarp.[15] We fit the diffractograms by usingthe powder diffraction files (International Center of Diffraction Data) of native cellulose (cI), arabinose (Ab), xylose (Xy) and cellulose II (cII). We do not find another component that lies in the studied region. Our fit agrees very well with previously reported results by Hespell.[16]

The comparison between the diffractograms of the subsequent samples presented in Fig. 2, show changes in shape[11] that confirms the cII presence, indicating that in certain moment of the process, extended swelling, followed by crystalline zones disruption and cellulose phase transition take place.[15]

For this reason, we deconvoluted all the diffractograms, and plot the variation of the relative areas of the diffraction peaks for cI, cII and Ab, with the *nixtamalization* time (Fig. 3). Xy was not taken into account because its low intensity. It can be seen that Ab tends to quickly disappear, while cI tends to increase. The cII peak appears about t_r = 188 min. This behavior is explained by the hemicellulose dissolution process that causes the apparent increase in the cI peak and by the cI-cII phase transition in the alkaline medium.[15,17] The inflection zone between t_r = 38 min to t_r = 188 min in the cI curve, signals the shift from inter- to intracrystalline swelling followed by the phase transition.

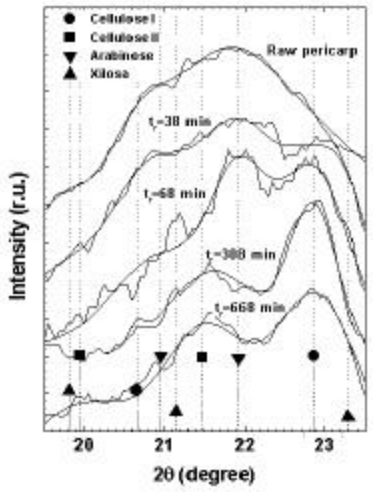

Fig. 2 X-ray diffractograms for pericarp taken at different *nixtamalization* times

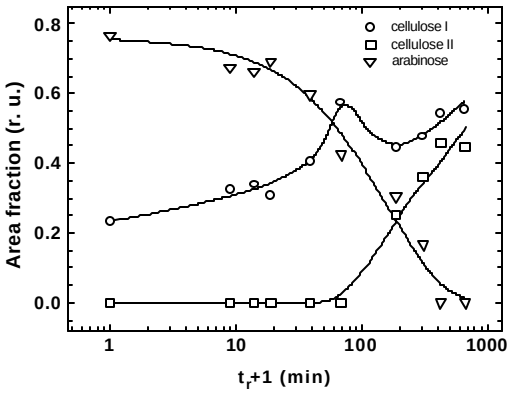

Fig. 3 Area fractions of the normalized native-cellulose, cellulose-II and arabinose peaks as function of *nixtamalization* time.

Crystallinity and thermal diffusivity

The variations of the total, crystalline and amorphous areas in the diffractograms with the nixtamalization time are shown in Fig. 4. The amorphous area variation illustrate the hemicellulose alkaline-dissolution and the hot-water-soluble components dissolution processes[18] as well as the disordering of the cellulose structure near the cI-cII phase transition and the existence of a non-soluble hemicellulose fraction. On the other side, the crystalline area variation is explained by the dissolution of the crystalline neutral sugars (Ab and Xy), combined with a competition between the degradation of the cI chain ends by extended swelling versus the stopping reactions and the formation of a stable compound (alkali cellulose),[15] that will lead to cII in the steeping stage.

From the crystalline and total areas under the diffractograms[19] we calculated the pericarp crystallinity (χ_c) shown in the Fig. 5.

The crystallinity reflects the whole changes that take place at the pericarp. The cooking stage consists mainly of the cutin and hemicellulose attack by alkaline hot-water combined with alkaline cellulose formation.[15,18,20] From the end of cooking to t_t = 188 min, a disordering of the material takes place, while the cI-cII phase transition is on run.[15] Finally, a well ordered structure, with the highest

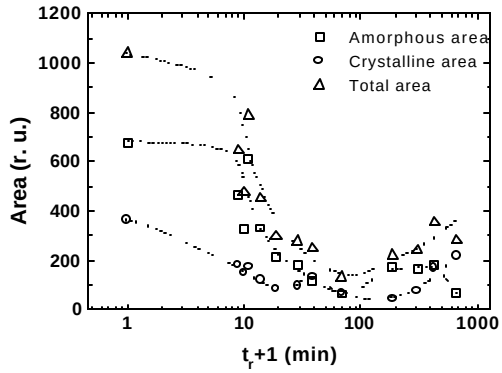

Fig. 4 Behavior of the amorphous, crystalline, and total areas of the x-ray diffractograms as function of the *nixtamalization* time.

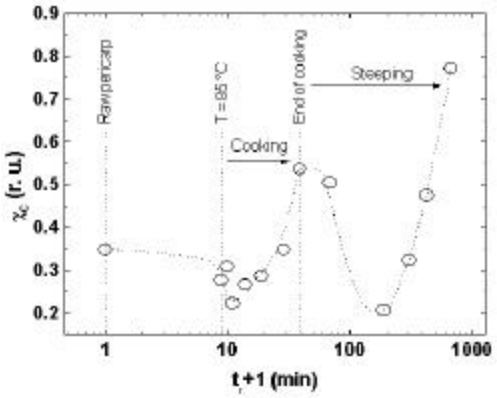

Fig. 5 Crystallinity of *nixtamalized* corn pericarp taken at different times of the same process.

crystallinity is obtained. The crystallinity for the raw pericarp was found to be $\chi_c \cong 0.35$, showing no variation with the maturity of the grain.

The behavior observed for the crystallinity is very similar with that obtained when the thermal diffusivities (α) were calculated, as can be seen in Fig. 6. For the raw pericarp, a value $\alpha \cong 4x10^{-4}$ cm^2/s was estimated. The behavior of the thermal properties show that better-crystalline structures such as cII would play the major role in the heat transmission, and that the amorphous components cause an scattering effect, that induces lower α values.[5]

However, we do not find linear relationship between the crystallinity and the thermal properties, as been reported by Alvarado-Gil *et al*.[5] In the figure 7 the lines represent only tendencies, not fitting. It can be seen that the points are quite dispersed, showing a complex behavior that confirms that the *nixtamalization* process involves a series of processes, each one affecting the resultant pericarp properties.

Morphological modifications

In the Fig. 8 we show the images obtained by SEM and AFM on the raw pericarp. The AFM images are the first reported for corn pericarp. From the highest magnification

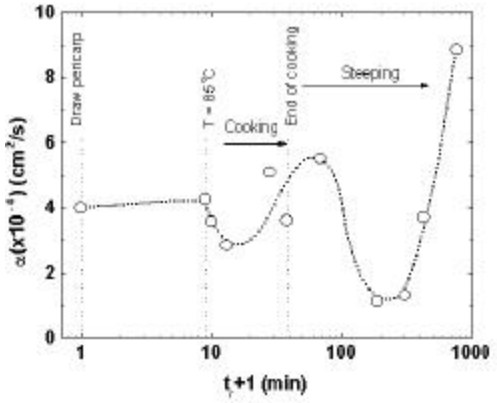

Fig. 6 Thermal diffusivity of the corn pericarp at different *nixtamalization* times.

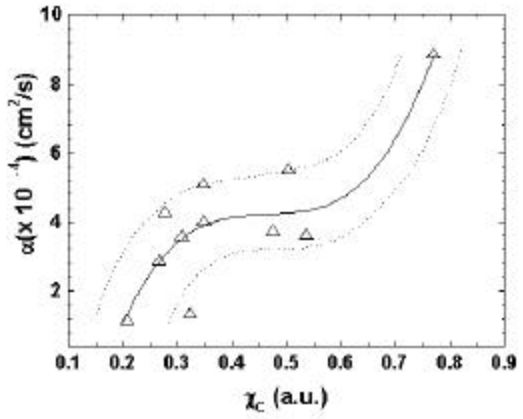

Fig. 7 The relationship between the thermal diffusivity and crystallinity of the *nixtamalized* corn pericarp.

it can be appreciated the fibrilar structure of the pericarp below the waxy cutin. The cutin rounded grains can be seen in the 10 x 10 μm^2 AFM image. The particle showed in the 10 x 10 μm^2 image is a corn-dust particle. This dust causes great difficulties in the AFM measurements, because the tip drags it all through the scanned area, giving scratched, dirty images.

From the 50 x 50 μm^2 3-D AFM image shown in Fig. 9 we estimated the fiber diameter of the raw corn pericarp about 5 μm thick, similar to corn pericarp tissues observed by Mongeau *et al*.[21] In the figure can also be appreciated that the dust particle is constituted by pyramid-like structures, that suggest it may be a sugar particle.

We appreciate extensive changes from the raw pericarp to that taken at the beginning of the isothermal cooking process (Fig. 10). In the 100 x 100 μm^2 set of images can be appreciated an increase in the fiber diameter that indicates water absorption or swelling.[15] The relief of the fiber in the cooked sample is also more pronounced. The waxy cutin rounded grains shown in the 5 x 5 μm^2 image had disappeared, being replaced by a rough surface, with pyramidal-like structures spread all over the image. These phenomena can be attributed to an early dissolution process

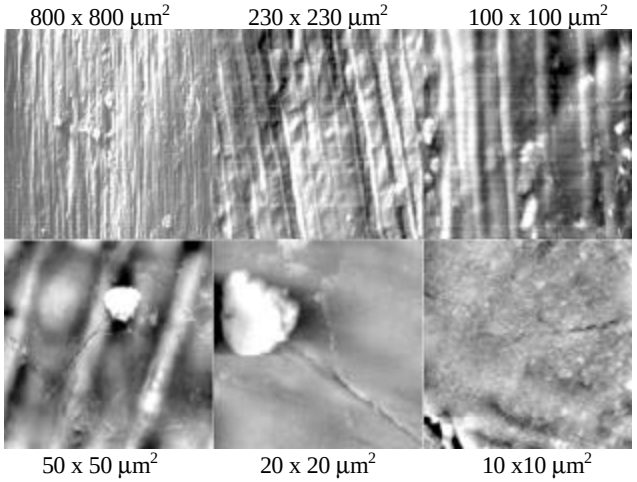

Fig. 8 SEM (a) and AFM (b) images of raw corn pericarp at different magnifications (upper images are SEM and lower AFM)

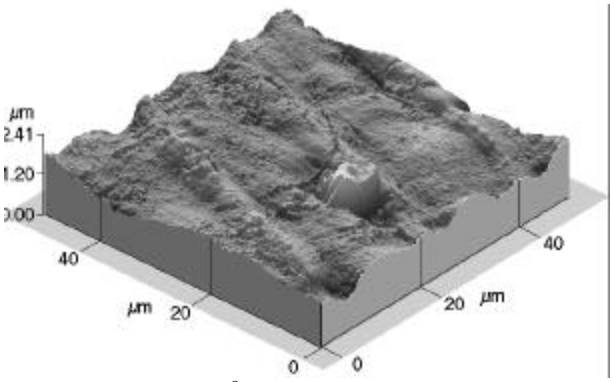

Fig. 9 3-D AFM 50 x 50 μm^2 image showing the fibrillar structure of the raw corn pericarp.

of the hemicellulose and cutin. The pyramids suggest a polycrystalline, ordered structure that could be a sugar such as arabinose or evenly, cellulose crystal edges.[22]

The evolution of the pericarp morphology during the isothermal cooking stage shows (Fig. 11a) that pericarp hemicellulose get dissolved and the surface seems more eroded as the *nixtamalization* time increases. Swelling is appreciable in extended degree from t_r = 13 min, when the surface fibers begin to twist.[23] From this point, the extended swelling of the fiber causes that it chain ends begins to dissolve, but there exist a competition between dissolution and recrystallization in the alkaline cellulose compound.[15] The 20 x 20 μm^2 image of t_r = 38 min shows a surface full of regular islands. These islands could be associated with alkaline cellulose crystallites. In the steeping stage (Fig 11b) at t_r = 68 min a fibrilar structure is noted, with portions of non-ordered material spread over the surface. The aspect of these zones suggests that they could consist of precipited or recrystallized material. Eroded surfaces are seen from the 20 x 20 μm^2 image. The observed reorganization could be due to the increase in the swelling power of the solution at room temperature,[24] that causes the fibers get aligned again. Another explanation could be an extensive dissolution of the hemicellulose that made appear the inner layers of the pericarp. This also explain the highly eroded surfaces. Extended swelling is noticed in t_r = 188 min, when the surface has extensive loosening of its fibrillar structure, however the 20 x 20 μm^2 image shows organized microstructure, very similar to that of t_r = 8 min. The image shows pyramids emerging from the matrix. These structures could be evidence of peeling of the cellulose chains. The surfaces of the other specimens (t_r = 338 min and 428 min) do not show great erosion, but they tend to be flat without identifiable features, corresponding to the observations reported by Muñoz-Hernández et al.[11] The more cooked sample, t_r =668 min, shows a surface very similar to that of t_r = 38 min that is, eroded zones covered with little and regular islands. At this point of the process, a new compound could be formed, the alkaline cellulose II.[15] It is expected that more steeping time lead to complete dissolution of the pericarp. In fact, this effect has been reported when higher $Ca(OH)_2$ concentrations are used, that corresponds with higher steeping times.[10-11]

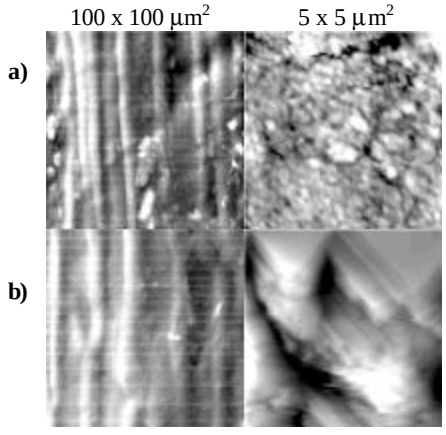

Fig. 10 Comparison between a) unprocessed pericarp and b) a pericarp taken at the beggining of the isothermal cooking stage of the *nixtamalization* process (t_r = 8 min). Left images are SEM, right are AFM.

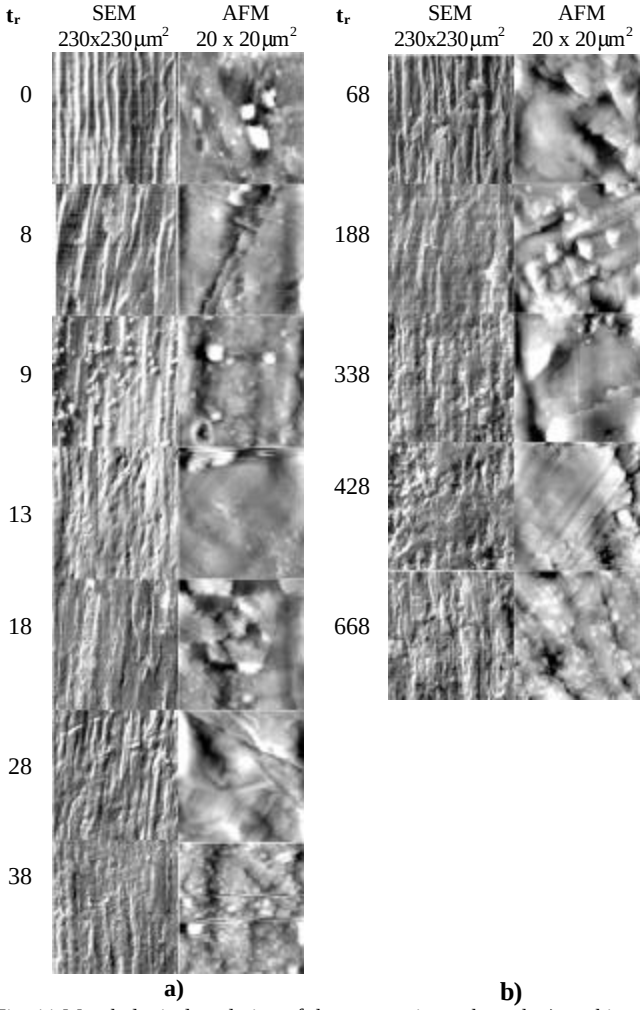

Fig. 11 Morphological evolution of the corn pericarp through a) cooking stage and b) steeping stage in the same *nixtamalization* process. 230 x 230 μm^2: SEM images, 20 x 20 μm^2: AFM images; t_r in minutes.

Conclusions

We studied the changes that the corn pericarp suffers during a typical *nixtamalization* process by using XRD, PA, SEM and AFM. We propose a model for the *nixtamalization* process that explains very well the observed changes in the chemical composition, crystalline structure, thermal diffusivity and morphology. Finally, we obtained some consistent values for physical properties of the raw corn pericarp: $c_c \cong 0.35$; $\alpha \cong 4x10^{-4}$ cm^2/s; fiber diameter $\cong 5$ µm.

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