CP-CT-8

CELLULOSE I TO CELLULOSE II TRANSITION IN EXTRACTED CORN PERICARP OBSERVED BY X-RAY DIFFRACTION

Álvaro Zapata-Navarro*, Felipe Caballero-Briones, Juan L. Peña Chapa and Augusto A. Iribarren Alfonso[(1)].
CICATA-IPN, Unidad Altamira, Km. 14.5 Carretera Tampico-Puerto Industrial Altamira, AP 165 89600 Altamira Tamaulipas, México. Email: zapata04@hotmail.com
[(1)] Instituto de Materiales y Reactivos, Universidad de La Habana, Vedado 10400 La Habana, Cuba.

Abstract

We studied by x-ray diffraction the phase transition of cellulose I to cellulose II in corn pericarp after extracting raw pericarp with H_2O, NaOH, $NaClO_2$ and KOH. By using a previously proposed method, we substract the amorphous components of the samples and deconvolute the cellulose I and cellulose II contributions from the KOH extracted pericarp spectrum. We found that even after KOH extraction an amount of the amorphous component of pericarp remains intact and that the observed crystallinity reduction in CI+CII sample is due to the phase transition disordering effects.

The study of physical and chemical properties of corn pericarp is very important to improve the products obtained from. Corn pericarp has been studied and showed to be composed of hemicelulloses A, B and C, cellulose I, lignin, starch, fat and protein.[(1)] As we have shown, after extraction with H_2O-NaOH-$NaClO_2$ hemicellulose-related amorphous components are partially solubilized and a high crystalline, cellulosic residue is obtained.[(2)] This method only solubilizes the components and does not induce any chemical or phase tranformation of the material.[(2)] On the other hand, cellulose I to cellulose II phase transformation of pure cellulose in the presence of a strong alkali such a KOH is a well known phenomena, although have not been observed or discussed in studies of composition of vegetables by extraction. In this work, our aim was to treat the pericarp cellulosic residue with 18 % KOH to transform the pericarp cellulose I to cellulose II and to extract the remaining amorphous components.

Corn pericarp insolubles from a previously described sequential extraction DI H_2O-NaOH-$NaClO_2$ [(2)] were treated with KOH 18% by 15 h at 25 °C. The non-soluble material was rinsed, neutralized, dehydrated and properly collected without perform a milling to avoid changes in the material by friction heating. Samples were analyzed by X-ray diffraction in a Siemens D5000 diffractometer using the Bragg-Brentano geometry. The normalized diffractograms of the raw (RP), $NaClO_2$-(CIR) and KOH-extracted (KIR) samples, and of commercial microcrystalline cellulose (MC) are shown in the Fig. 1. The A-marked zones are related with the amorphous hemicelluloses that diminish after the $NaClO_2$ extraction. [(2)] The CIR spectrum is almost composed by cellulose I, as

compared with the MC. The observed variations in the relative intensities of the peaks are related with changes in particle sizes. In the KIR diffractogram can be observed the aparition of a peak about 12° marked as C-II. It can also be observed that the width of the main peak about 22° increases with the KOH extraction. Fig 2 shows the KIR diffractogram after substraction of the amorphous contributions. From this spectrum, we substracted the crystalline contribution of CIR and obtained a spectrum of cellulose II (CII), as reported by Moharram et al.[3]

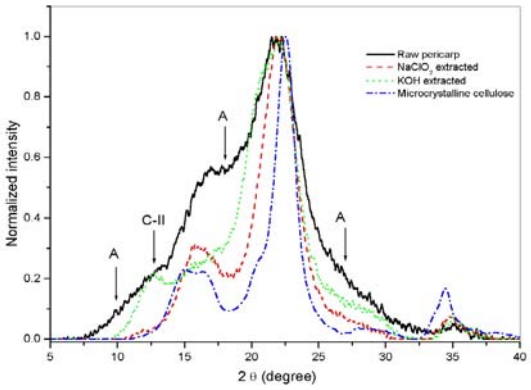

Fig. 1. Normalized X-ray diffractograms of RP, CIR, KIR and MC

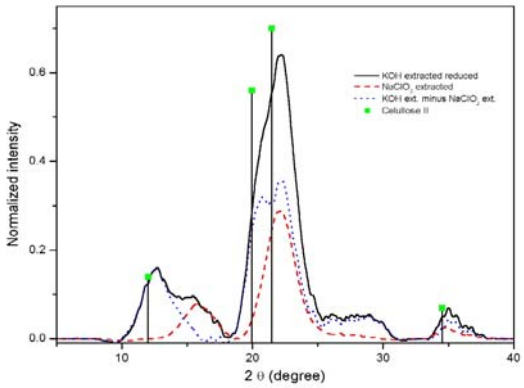

Fig. 2. KIR reduced spectra showing CII.

We calculated the crystallinity of the samples as previously reported and the results are shown in Table I. The crystallinity of KIR diminishes with respect to that of CIR. This is readily explained in terms of the phase transition related disorder. Again can be seen that the use of parabolic functions to substract the amorphous components induces great variations with respect to our method.

In summary we find by x-ray diffraction that cellulose I was partially transformed to cellulose II and that some amorphous fraction remains in the residue partially due to the disordering caused by the phase transition.

Table I. Crystallinity of the samples.

Sample	Crystallinity index[a]		Difference (percent)
	Our Method	Traditional	
MC	75.5	68.3	11
RP	31.6	15.4	105
CIR	59.4	52.4	13
KIR	47.2	38.9	21

[a] X = Crystalline area/ Total area x 100 (areas under diffractograms)

Acknowledgements.

This work was supported by CGPI-IPN.

References

(1) M. Sugawara, T. Suzuki, A. Totsuka, M. Takuechi, and K. Ueki, Starch/Stärke **46,** (1994) 335-337.

(2) A new method to obtain the crystallinity of corn pericarp, F. Caballero-Briones, A. A. Iribarren, J. L. Peña, and Á. Zapata-Navarro, presented at SLAP 2002.

(3) M. A. Moharram, T. Z. Abou El Nasr, and N. A. Hakeem, J. Polym. Sci. 19, (1981) 183-187.