

X-RAY DIFFRACTION PATTERN AND RELATIVE CRYSTALLINITY OF IRRADIATED ARROWROOT STARCH

Aline G. Barroso, Rafael H.L. Garcia, Nelida L. Del Mastro

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
nlmastro@ipen.br

ABSTRACT

After cereals, tubers and roots are the major source of starch for food and industrial uses. Arrowroot refers to any plant of the genus *Marantha*, but the term is most commonly used to describe the easily digested starch obtained from the rhizomes of *Marantha arundinacea*. The rhizomes of this herbaceous plant contain about 20% of starch. As few studies exist on arrowroot starch, the objective of this preliminary work was to study the X-ray diffraction patterns (XRD) patterns of arrowroot starch when treated by γ -radiation with doses up to 15 kGy in a ^{60}Co source. The XRD patterns of the arrowroot starch exhibited A-type crystalline arrangements with strong peaks at approximately 15°, 17°, 18° and 23° (2 θ). A slight increase of diffractogram peaks intensity was noticed after the irradiation process. The crystallinity index was calculated using Bruker DIFFRAC.EVA version 4.2 software. Relative crystallinity seems to increase with radiation doses, and this effect is more noticeable at low doses. That can be attributed to different radiation sensitivity among the amorphous and crystalline regions of the arrowroot starch molecule. Present results will contribute to elucidate the behavior under radiation treatment of this starchy component increasingly employed by the food industry.

1. INTRODUCTION

Starch is constituted of two biopolymers, amylose, essentially a linear macromolecule, and amylopectin, a highly branched macromolecule. These two biopolymers form a semicrystalline structure in the starch granule, which consists of crystalline and amorphous lamellas [1]. Starches from different botanical origin vary in total starch and amylose content. Original from tropical regions of South America, arrowroot (*Marantha arundinacea*) also called araruta, is the flour made from the tuber of the same name. Brazilian Indians believed that araruta neutralized the poison used by the enemies [2]. In cookery it is used for thickening sauces and in cakes, cookies and desserts. Today, we know that the arrowroot tuber extracts have immunostimulatory effects in vivo and in vitro [3] and it is effective in disease prevention and a useful biomedical source material [4-6]. Also, arrowroot starch is starting to be used as polymer matrix in the production of biodegradable films [7]. According to Gordillo et al. [8], arrowroot starch exhibited high purity (starch content >99%) with an amylose content >40%.

X-ray diffraction (XRD) is a nondestructive technique used to identify and quantify crystalline and amorphous phases in solids. As few studies exist on arrowroot starch, the

objective of this preliminary work was to study the XRD patterns of arrowroot starch when treated by ionizing radiation.

2. EXPERIMENTAL

Samples of arrowroot or araruta were obtained in bulk from local food market as a fine powder. The starch were gamma irradiated at doses of 0 - 15kGy, dose rate about 1 kGy/h, using a ^{60}Co Gammacell 220, Atomic Energy of Canada Ltd (AECL) in polyethylene bags at room temperature, dose uniformity factor of 1.13. Data of X-ray diffraction were acquired from a Bruker D8 diffractometer, using $\text{Cu-}\alpha$ radiation, two theta from 5 to 37° , stepsize of 0.04° and 10 seconds per step. The crystallinity index (CI) was calculated using the Bruker DIFFRAC.EVA version 4.2 software. To avoid the contribution of amorphous from the sample holder (usually made of glass), an aluminum sample holder was used. To improve accuracy, each sample was analyzed 5 times using different quotas of sample.

The first step for CI determination was to subtract the background, which has contributions due to incoherent and air scattering, electronic noise and other unwanted signals. To accomplish this step, a XRD of aluminum plate (that is virtually free of amorphous material) was carried out, and its background signal was subtracted from all diffractograms of this work (light blue line at figure 1). The second step was the determination of the amorphous fraction of the diffractograms, using the EVA software, using the parameters curvature and threshold equal to unity. This step created the green dashed line at figure 1. The last step was to integer the total area of the diffractograms (blue line at figure 1), subtract the amorphous area and divide by the diffractogram total area.

3. RESULTS AND DISCUSSION

XRD data for non-irradiated arrowroot is displayed in Fig 1. As can be seen, the X-ray diffraction patterns of the arrowroot starch exhibited A-type crystalline arrangements with strong peaks at approximately 15° , 17° , 18° and 23° (2θ) and weaker peaks at approximately 10° , 11.5° , 20° , 26.5° , 30.5° and 34° (2θ). This pattern is quite similar to the corn starch from the reference #39-1911 from the PDF catalog, with its peaks shown in red at figure 1.

The 20 diffractograms obtained in this work had very subtle visual differences. A crop of the top of the two stronger peaks of various diffractograms can be seen in detail in figure 2.

Data of relative crystallinity are displayed in Figure 3. Although the standard deviation of the results of the method is rather high, it is possible to observe that the increase of the applied radiation dose seems to raise the crystalline index of samples. This can be attributed to different radiation sensitivity among the amorphous and crystalline regions of the arrowroot starch molecule. However, this effect is negligible at the higher radiation doses used in this work.

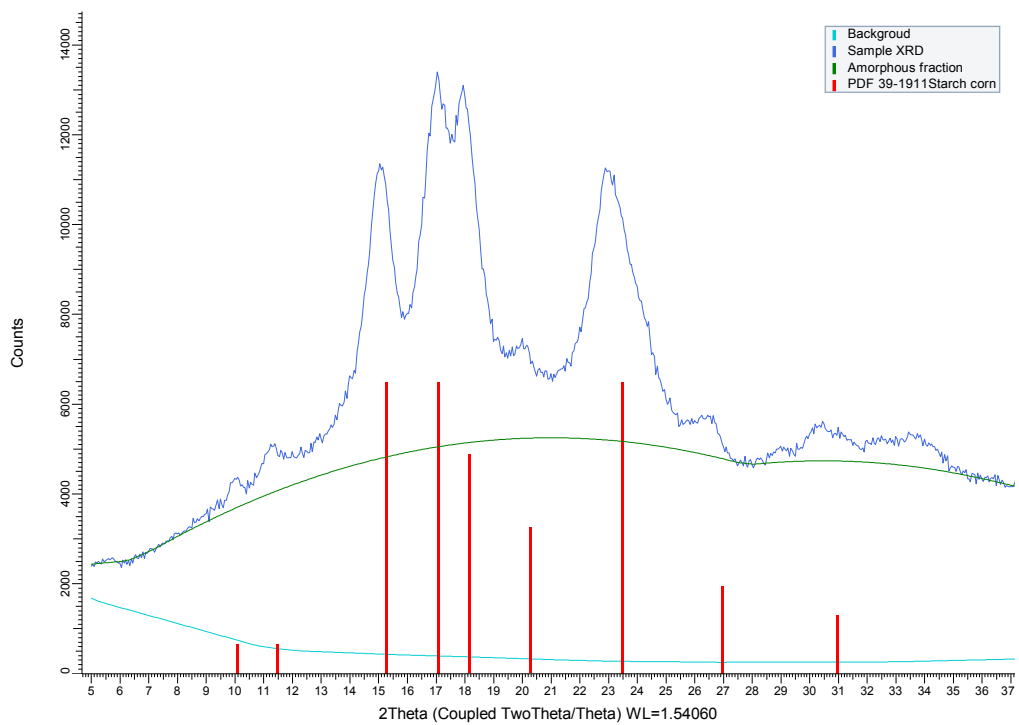


Figure 1: X-Ray diffractogram of non-irradiated arrowroot sample.

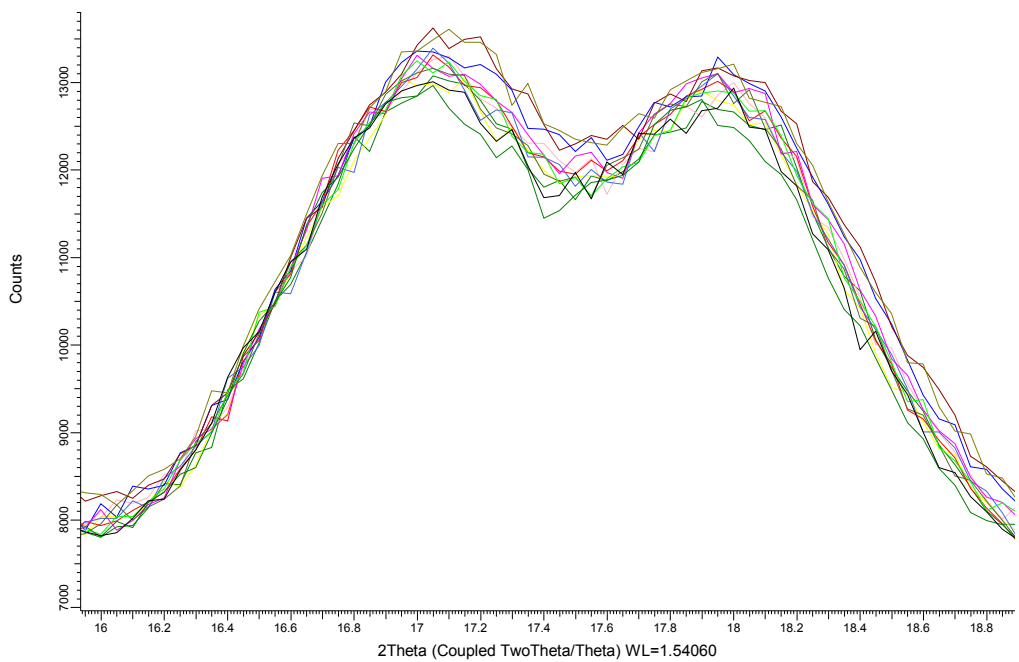


Figure 2: Detail of X-Ray diffractograms of arrowroot samples.

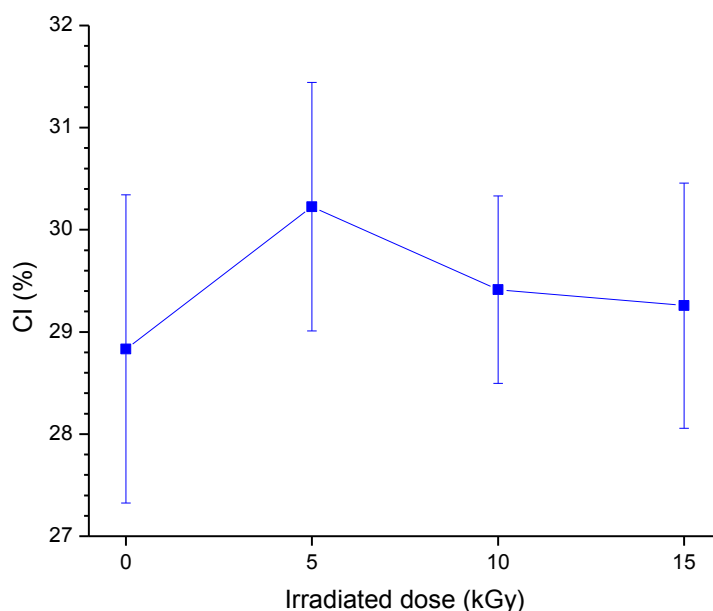


Figure 3: Average Crystallinity Index (CI) calculated from of arrowroot samples irradiated at different doses.

3. CONCLUSIONS

The crystalline content of arrowroot starch found in this study is within the expected range of common starches of 20-45%. In the present work, relative crystallinity apparently increased with irradiation, being this effect more noticeable at the lower dose assayed. As Pepe et al. [9] pointed out, some treatments can cause the rearrangement of amylose and amylopectin chains in the starch, and therefore may modify its X-ray pattern, crystallinity, swelling power, amylose leaching, pasting, and gelatinization properties, as well as its susceptibility to enzymatic or acidic hydrolysis. Also, different radiation sensitivity of the amorphous and crystalline regions of the arrowroot starch molecule can be expected. Present results will contribute to elucidate the behavior under radiation treatment of this starchy component increasingly employed by the food industry.

ACKNOWLEDGMENTS

The authors acknowledge Eng. Elizabeth Somessari for irradiation assistance.

REFERENCES

1. J. Jane J, T. Kasemsuwan, S. Leas, et al. Anthology of starch granule morphology by scanning electron microscopy. *Starch/Starke* **46**, pp 121–129 (1994).
2. M.B. Kijac. *The South America Table: The Flavor and Soul of Authentic Home Cooking from Patagonia to Rio de Janeiro*. The Harvard Common Press, Boston, MA (2003).
3. I.D. Kumalasari, E. Harmayan, L.Lestari, R. Arsanti, et al. Evaluation of immunostimulatory effect of the arrowroot (*Maranta arundinacea*. L) in vitro and in vivo. *Cytotechnology*, **64**, pp. 131-137 (2012).
4. U.G.Kalappura, R.Augustine, K.T.Mathew. Microwave properties of arrowroot and its medical applications. *Microw. Opt. Technol. Lett.* **51**, pp. 1267–1270 (2009).
5. M.Y.Lee, K.H.Chang. Effects of cheonggukjang containing arrowroot isoflavones on bone metabolism in ovariectomized rats. *Food Sci. Biotechnol.*, **20**, pp. 335–34 (2011).
6. S. Nishaa, M.Vishnupriya, J.M.Sasikumar, H.P.Christabel,V.K.Gopalakrishnan. Antioxidant activity of ethanolic extract of *Maranta arundinacea* L. tuberous rhizomes. *Asian J. Pharm. Clin. Res.*, **5**, pp. 85–88 (2012).
7. W. J. dos Santos, C.S. Miranda, A.P. B. Gonçalves, et al. Propriedades mecânicas de filmes obtidos a partir de fécula de araruta (*maranta arundinaceae*), nanoargila e glicerol. *Anais do 21º CBECIMAT - Congresso Brasileiro de Engenharia e Ciência dos Materiais*, 09 a 13 de Novembro de 2014, Cuiabá, MT, Brasil.
8. C. A. S. Gordillo, G. A. Valencia, R. A.V. Zapata and A. C. A. Henao. Physicochemical Characterization of Arrowroot Starch (*Maranta arundinacea* Linn) and Glycerol/Arrowroot Starch Membranes. *Int. J. Food Eng.*, **10** (4), pp. 727-735 (2014).
9. L. S. Pepe, J. Moraes, K. M. Albano, V.R.N Telis, C.M.L. Franco. Effect of heat-moisture treatment on the structural, physicochemical, and rheological characteristics of arrowroot starch. *Food Sc. Technol. Internat.*, **22**(3), pp. 256-265 (2015).