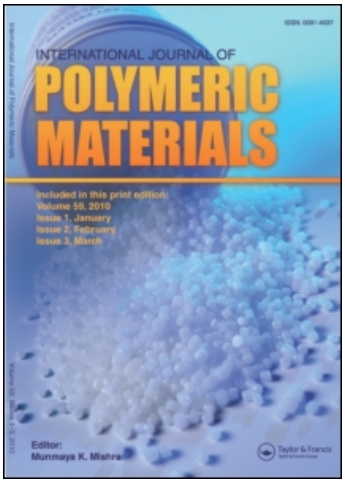

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NMR and X-Ray Studies of Starches Derived from Tropical Fruit Seed Gelatinization Process

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NMR and X-Ray Studies of Starches Derived from Tropical Fruit Seed Gelatinization Process

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Gelatinization of the starch obtained from fruit seed such as mango and cumbaru was investigated applying an analytic methodology developed in the polymer nuclear magnetic resonance (NMR) laboratory at IMA/UFRJ, employing high resolution nuclear magnetic resonance spectroscopy in the solid state for hydrogen nucleus, using ^{1}H HR-MAS pulse sequence. The results showed that NMR can be used instead of some techniques normally applied to study the gelatinization process, because ^{1}H HR-MAS and relaxation time allow the evaluation of this process at the molecular level. NMR was also able to indicate the best gelatinization conditions. To start this study the glass transition (Tg) determination was a first step, because the Tg of seed starches are different than the Tg of starches derived from cereal, for example. The ^{1}H HR-MAS NMR showed some useful information on the fruit seed starches gelatinization process. X-ray measurements were also used to support the data obtained from NMR technique. It was verified,

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from X-ray, that mango starch exhibits crystallinity in the **A** *form and cumbaru showed a predominant amorphous phase. The use of* ^{1}*H HR-MAS was shown to be a new, powerful method to follow the gelatinization process, because this process can be understood at the molecular level.*

Keywords: gelatinization, ^{1}H HR-MAS, starch

INTRODUCTION

Starch is formed as granules with low moisture percentage. The granules can absorb water and swell. However, the swelling is reversible and the degree of reversibility is very much dependent on the starch nature. At high temperatures an irreversible swelling is called gelatinization, which is a process that is normally employed to prepare flours. The gelatinization phenomenon is a process that changes in ordered system to a disordered one [1–4]. The starch granules gelatinization temperature is dependent on the specific starch nature. As an example, corn starch gelatinizes between 60 and 70°C [1–2]. It is known that each starch exhibits different granular densities, which affects the way the granules absorb water. In this process the hydrogen bondings between the starch chains start to break slightly [2–3]. Starches derived from fruit seeds do not present the same behavior as tubercles and cereals, because their gelatinization temperatures are higher. Few reports can be found on gelatinization process of starches that come from tropical fruits [5–7]. Also, they do not behave in the same way when comparing different fruit seeds [6–7]. To understand the fruit seed starches properties and characteristics such as cooking, brewing, textural, and digestive, the gelatinization process must be carefully studied, because this phenomenon provides information on the starch structure and manipulation, which are very useful for food preparation.

As the solid state NMR spectra are sensitive to the crystalline form of solids and can therefore be readily used to study polymorphism, and is also of substantial value for the study of amorphous and heterogeneous materials, as polysaccharides [4–5,8], the authors have chosen to use ^{1}H HR-MAS technique as an easy means of obtaining high resolution spectra for a variety of samples, comparing the results with X-ray patterns.

Thus, the focus of this work is to evaluate the gelatinization process of mango and cumbaru starches obtained from fruit seed, applying a combination of ^{1}H HR-MAS spectra and X-ray patterns, suggesting

them as a new rapid methodology to obtain the response of the behavior of the starch samples to the gelatinization conditions.

EXPERIMENTAL

The starches were obtained from the fruit seed after the delipidation process with hexane as a solvent, extracting for 24 h at the boiling point. The solvent was changed after each time until no more oil was being extracted, which was followed by solution ^{1}H NMR. The degree of starch purity was checked by ^{1}H HR-MAS technique, until only polysaccharide signals were detected. The starches were, dried in a circulating air oven to constant weight and were kept in a descicator to avoid water absorption.

In this work, several conditions were used in a method to prepare the gelatinized starches. The mango and cumbaru seed starches (with 8.4 percent of initial relative humidity) were suspended in water varying the solution concentration and the temperature of processing. The temperature chosen was based on the Tg values determined by differential scanning calorimetry measurements, the value of this parameter was around 150°C for both seed starches. Thus, four conditions were carried out in this process:

1. Starch concentration: 3% and temperature: 150°C.
2. Starch concentration: 5% and temperature: 150°C.
3. Starch concentration: 5% and temperature: 200°C.
4. Starch concentration: 10% and temperature: 150°C.

In the method used, the heating process was carried out with constant agitation, and after that all solutions were rapidly cooled in cold water to avoid retrodegradation. Then, acetone was added to each gel formed to help the water elimination, and the samples were kept at ambient temperature (26°C) for two hours. Then, these solutions were put in a vacuum oven at 70°C, for three days, to eliminate the water. The gelatinized samples were maintained in a dissector to avoid water absorption.

The X-ray diffraction patterns were obtained with a Rigaku miniflex diffractometer, operating at the Cu Kα wavelength (1.542 Å).

The ^{1}H HR-MAS NMR spectra were obtained in a BRUKER DRX 400 spectrometer operating at 400.13 MHz for ^{1}H, with a spinning rate at 12 kHz in the magic angle, using the following conditions: spectral width: 5669 Hz; acquisition time: 1.8 s; pulse width (45°): 5.9 μs; recycle delay: 1 s; number of transients: 128; type of processing: zero filling and without line broadening.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of native mango and cumbaru starches showed a typical behavior of non-ordered semicrystalline sample and a heterogeneous sample, respectively. The X-ray diffraction patterns of mango starch seed showed to be predominately **A** form and the degree of crystallinity of this starch could not be determined, in spite of a large amorphous region (Figure 1a). The profile of X-ray diffraction of cumbaru starch seed (Figure 1b) shows larger amorphous halo, comparing to mango starch X-ray profile, showing that this starch is an amorphous heterogeneous sample.

As was shown in the Experimental section, the gelatinization study was done at four different process modes, and they were accompanied by both X-ray and ^{1}H HR-MAS techniques. The X-ray diffraction patterns of mango starches after each type of gelatinization mode can be seen in Figures 2a, b and 3a, b. From the X-ray diffractogram, the better gelatinization temperature was about 150°C. It was also observed from the X-ray profile that both process 2 and 4 generate a better gelatinized starch than the other two. For the process 1 and 3 a complex V was formed.

The ^{1}H HR-MAS spectra were recorded as a new and nondestructive technique to evaluate the chemical order before and after gelatinization process. Both ^{1}H HR-MAS spectra of mango and cumbaru seed starches showed a pattern of semi-crystalline compound with an amorphous phase. For both fruit seed starches, the ^{1}H NMR signals were located at 5.2 ppm, relative to the hydrogen linked to anomeric carbon and a wide signal from 3.6 to 4.6 ppm attributed to the hydrogens linked to C**H**$_2$−OH and C**H**−OH groups.

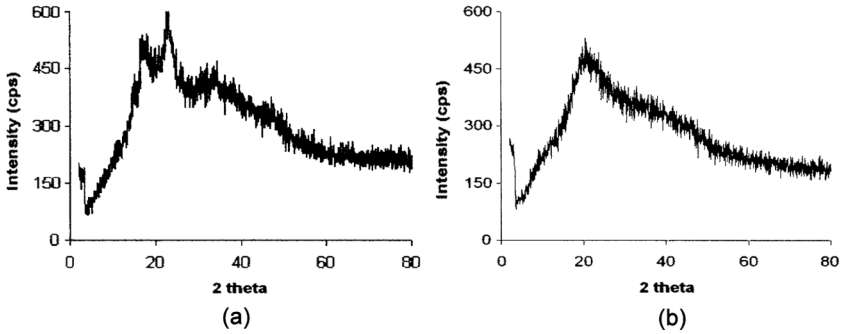

FIGURE 1 Diffraction pattern of native mango starch and native cumbaru starch.

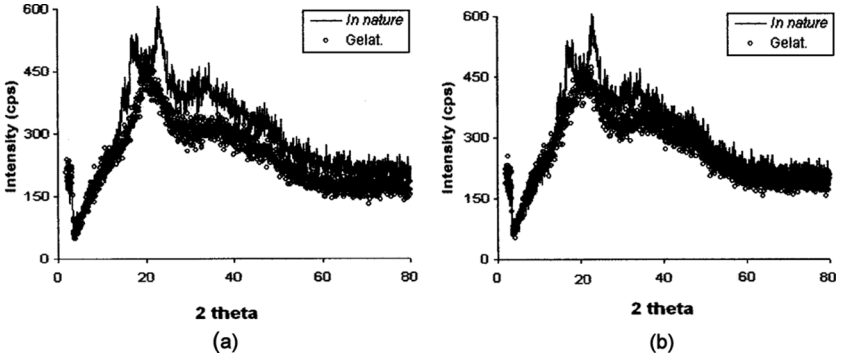

FIGURE 2 Diffraction pattern of native mango starch compared to mango starch gelatinized by process 1 (a) and process 2 (b).

The gelatinization process of mango starch was also accompanied by ^{1}H HR-MAS. During this process the crystallinity is changed, water is adsorbed onto the surface of the granule, and the hydrogen bonding between the starch polymers within the granule might begin to be loosened slightly. This allows the water to penetrate into the granule. At this point, the starch granule is swollen as much as possible, and, as a consequence, the chains disorder increases and the sample heterogeneity also increases causing a shortening in the length of spin-spin relaxation time (T_2), evidenced by a decrease in the signal resolution, which is wider than the native starch signals. The ^{1}H HR-MAS spectra of those gelatinization processes are exhibit in Figures 4 to 7. From

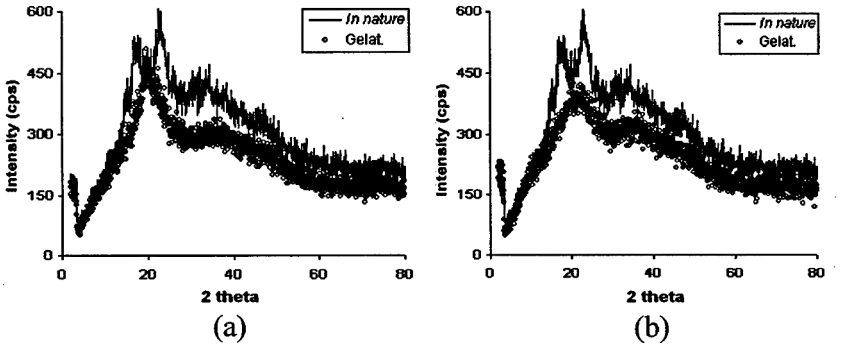

FIGURE 3 Diffraction pattern of native mango starch compared to mango starch gelatinized by process 3 (a) and mango starch gelatinized by process 4(b).

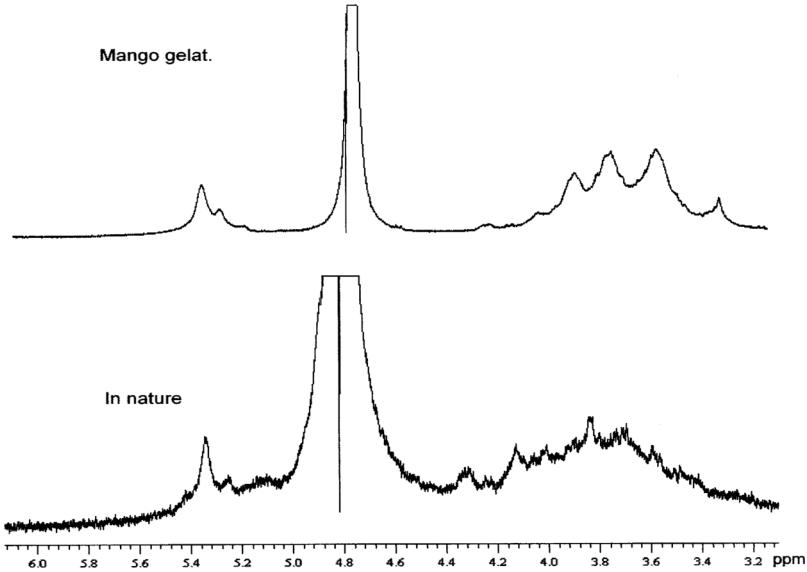

FIGURE 4 ^{1}H HRMAS NMR spectra of native mango starch compared with mango starch gelatinized by process 1.

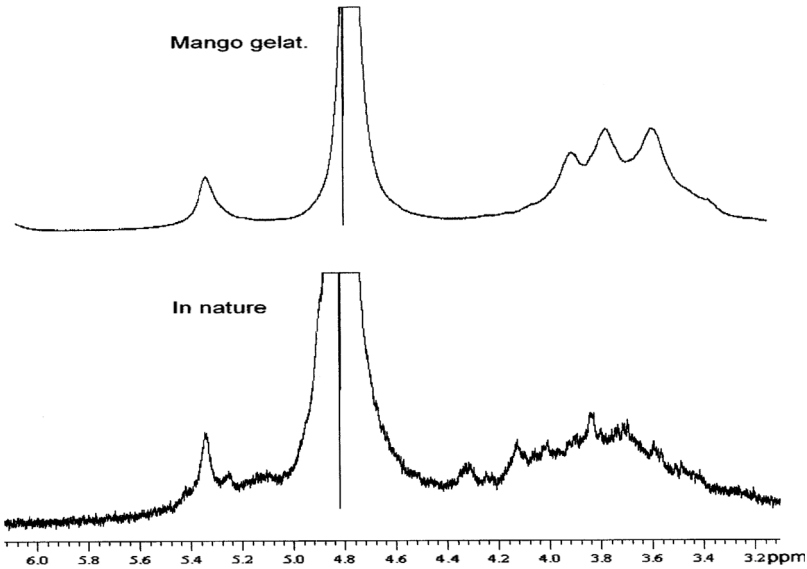

FIGURE 5 ^{1}H HRMAS spectra of native mango starch compared with mango starch gelatinized by process 2.

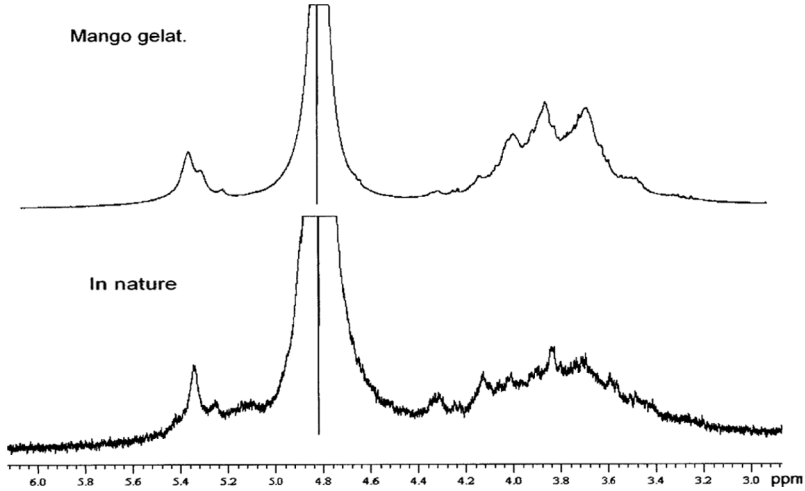

FIGURE 6 ^{1}H HRMAS spectra of native mango starch compared with mango starch gelatinized by process 3.

those NMR spectra a loss of ^{1}H signals resolution after gelatinization process can be seen compared to native starches. The evaluation of those gelatinization processes indicates that process 2 is more efficient

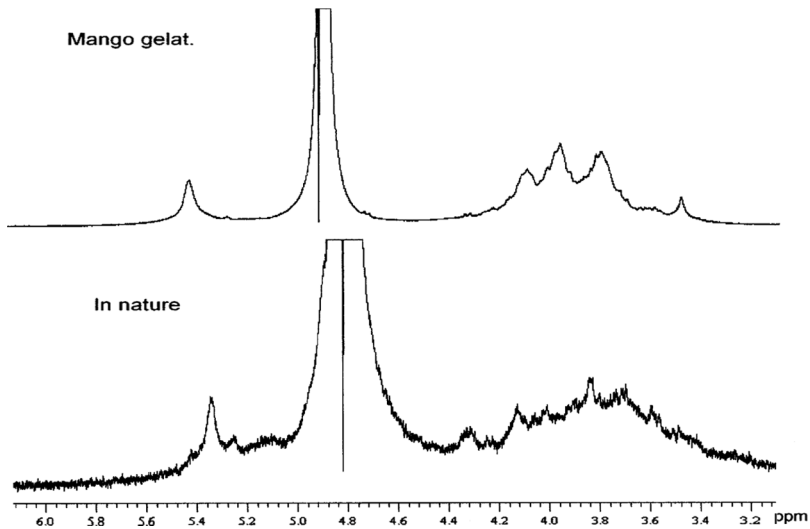

FIGURE 7 ^{1}H HRMAS spectra of native mango starch compared with mango starch gelatinized by process 4.

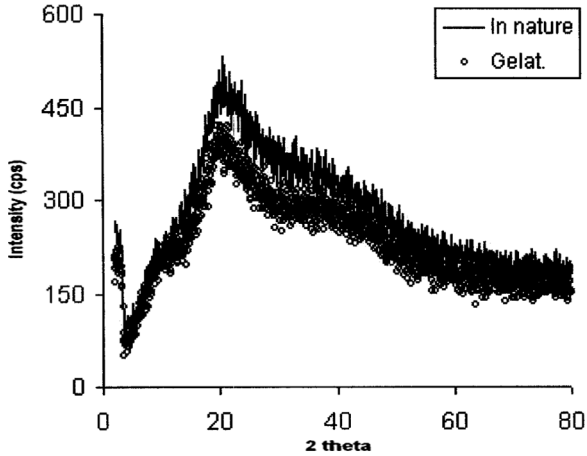

FIGURE 8 Diffraction pattern of native cumbaru starch compared to cumbaru starch gelatinized by process 2.

than the others, because of the higher loss in the ^{1}H NMR signals together with the increased amorphous phase.

The cumbaru starch gelatinization was carried out on the basis of mango starch gelatinization results. Thus, only process 2 was applied to the cumbaru starch, because this process was the most efficient for mango starch seed. The cumbaru diffraction patterns (Figure 8) and

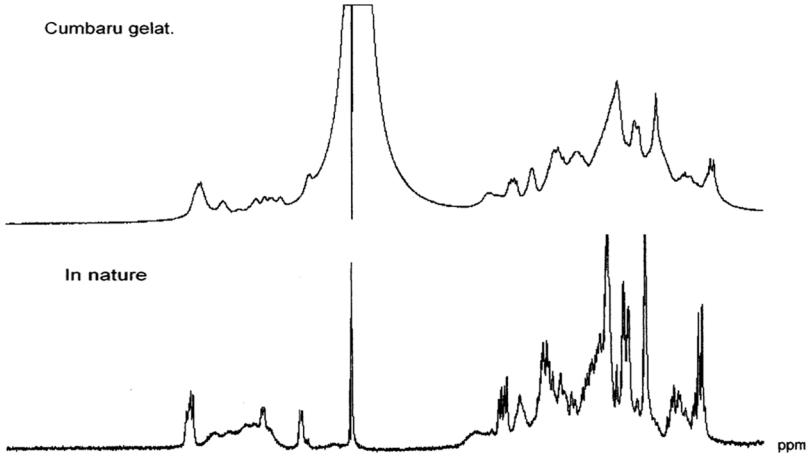

FIGURE 9 ^{1}H HRMAS spectra of native cumbaru starch compared with gelatinized cumbaru starch.

the ^{1}H HR-MAS NMR spectrum of the gelatinized sample showed that the gelatinization process was also very efficient for the cumbaru seed starch. Figure 9 shows a comparison of ^{1}HR-MAS spectra from native and gelatinized cumbaru seed starch. Comparing both spectra, a big loss of signals resolution is evident, as a consequence of the crystallinity loss, causing an increase in the amorphous region, which is evident in the base of the signals and confirms the efficiency of the gelatinization process developed for the fruit seed starch.

CONCLUSIONS

The ^{1}H HR-MAS was able to define the better gelatinization process conditions for the fruit seed starches studied. It was also shown to be a good method to accompany this process, because it permits understanding, at the molecular level, the response of whole sample behavior.

It could also be evidenced that NMR is a very strong spectroscopy tool, which allows one to complement the data obtained by other techniques and has a great importance in many studies.

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