

Effect of Aging on the Microstructure of Plasticized Cornstarch Films

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Abstract: Aging of cornstarch films prepared by casting was investigated. Water and glycerol-plasticized cornstarch films were stored at 50% relative humidity over a period of 330 days. Aging was followed by X-ray diffraction (XRD) and atomic force microscopy (AFM). XRD spectra indicated development of B-type crystallinity even for fresh films and that the crystallinity index increased from 0.06 to 0.28 as a function of storage time. AFM images of 270-day-old films revealed that the general morphology and the overall roughness have not changed due to aging. AFM phase contrast images at higher magnification showed an increasing number of ordered domains at the surface of these films, which may be attributed to recrystallization of amylose. No morphological change was observed at least at the surface of the granular region, which is enriched in amylopectin.

Keywords: *Cornstarch films, Aging, Atomic force microscopy, X-Ray diffraction.*

Introduction

Due to its excellent biodegradability, low cost and worldwide availability from a large number of crops, starch is considered an attractive source for bioplastics production^[1]. Starch is composed of two polysaccharides, amylose and amylopectin. Amylose is mostly linear whilst amylopectin is highly branched. Starch occurs as semicrystalline granules with varied sizes and shapes in grains, roots and tubers. The granule crystallinity is associated with the amylopectin linear chains and may give different X-ray diffraction (XRD) patterns, depending on the starch source. Cereal starches produce an A-crystalline pattern (monoclinic lattice) with densely packed double helices in the unit cell^[2]. Potato and certain tuber starches give a B-crystalline pattern (hexagonal lattice) in which the double helices packed in parallel fashion are combined with structured water^[3]. C-type pattern occurs in certain legume starches and is thought to be an intermediate structure of the A- and B-types.

Native starch may be converted into thermoplastic materials by conventional methods (extrusion, injection-molding) in the presence of plasticizers, such as water and low molecular weight polyols. The casting technique can also be applied. In this case, starch is processed by heating in the presence of excess of water, which causes irreversible swelling of the granules. Swelling is accompanied by disruption of the native crystalline structure and solubilization of amylose. This phenomenon is known as gelatinization^[4].

The two main drawbacks to the more extensive use of starch as a thermoplastic are the sensitivity of its properties

to fluctuations in water content and its physical aging^[4,5]. The latter is associated with time-dependent changes in properties, including their mechanical^[6] and diffusional behaviors^[7].

It has been reported that extruded starch at ambient moisture contents of 10-50% gradually becomes more brittle with time^[8]. Data from differential scanning calorimetry and dynamic mechanical analysis indicated that embrittlement of gelatinized starch can occur as a result of free volume relaxation during sub- T_g aging as well as a result of plasticizer loss by evaporation. Some authors verified that there were marked changes in the stress-strain behavior of films formed by thermoplastic barley and oat starches during 2 months of storage. It was concluded that crystallization and/or reorientation of amylose and amylopectin caused the aging. The authors also observed that even though occurring during longer storage times, the changes visualized in thermoplastic starches are very similar to retrogradation of normal starch gels^[6].

In the present work, X-ray diffraction (XRD) and atomic force microscopy (AFM) were used to investigate the effect of aging on the microstructure of plasticized cornstarch films stored at intermediate relative humidity.

Materials and Methods

Preparation of films

Food grade cornstarch, composed of 26 - 30% amylose and 74 - 70% amylopectin, and with less than 0.5% gluten was supplied by Corn Products Brazil (São Paulo, Brazil).

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Cornstarch (5 g) was dispersed in 50 ml distilled and deionized water at room temperature. Suspensions were diluted with 50 ml water previously heated to 95 °C and then kept under stirring and reflux conditions for 5 min. Glycerol (0,75 g) was added as a plasticizer. The hot suspensions were poured onto polyethylene Petri dishes and allowed to dry at 50°C for 12 h. Films were peeled off and conditioned at 50% relative humidity (RH). The thickness of the films (70 – 100 μm) was measured with a digital micrometer (Mitutoyo n° 293-265, Mitutoyo Corporation, Japan). The water content of the films was evaluated by drying the samples in an oven at 50 °C to constant weight.

Atomic force microscopy (AFM)

A Topometrix Accurex IIL (Topometrix, Santa Clara, USA) instrument, equipped with a noncontact AFM probe head and a 100 μm Tripot scanner was used to image the samples. The tips (Topometrix 1660™) were made of silicon and mounted on a cantilever with a spring constant of ca. 40 N/m and resonance frequencies in the 100 - 150 kHz range. Scanning was carried out at the free cantilever oscillation frequency and different amplitudes, depending on the stability and contrast obtained. The amplitude was set higher than 80 nm and the set point was fixed at 10 to 30% of the free oscillation amplitude in order to guarantee that the microscope was operating in intermittent contact mode. Samples were fixed on double-coated adhesive tapes and the AFM images of the upper surface were obtained in air. Changes in the sample vertical position are presented as height images. Changes in the phase angle difference between the oscillations of the cantilever and the standard signal, which drives the piezoelectric crystal during the intermittent contact mode, are presented as phase images.

X-Ray diffraction (XRD)

X-ray diffraction patterns were recorded on a Miniflex diffractometer (Rigaku Corporation, Japan) operating at CuKα wavelength of 1.542 Å. Data were acquired in the angular region (2θ) of 2-30° (step size of 0.05°, measuring 1 s per step). Diffractograms were smoothed with Savitsky-Golay filter, 7 points, and the baseline was corrected by drawing a straight line between the intensities at (2θ) 3.5 and 30°. The height (H_c) of crystalline diffraction at $2\theta = 17^\circ$, which corresponds to the distance between the crystalline peak and the amorphous curve, was measured relatively to the height of the peak as measured from the baseline (H_t). The B-type crystallinity indices related to the peaks at approximately $2\theta = 17^\circ$ ($X_{c,B-17^\circ}$) was calculated dividing H_c by H_t [5]. The B-type crystallinity index related to the peak at approximately $2\theta = 22^\circ$ ($X_{c,B-22^\circ}$) and the V_H -type crystallinity index ($X_{c,VH}$) related to the peak at approximately $2\theta = 20^\circ$ (2θ) were calculated according to the same method.

Results and Discussion

Aging of cast cornstarch films, stored at 50% RH, was investigated over 330 days. Due to the low thickness of the

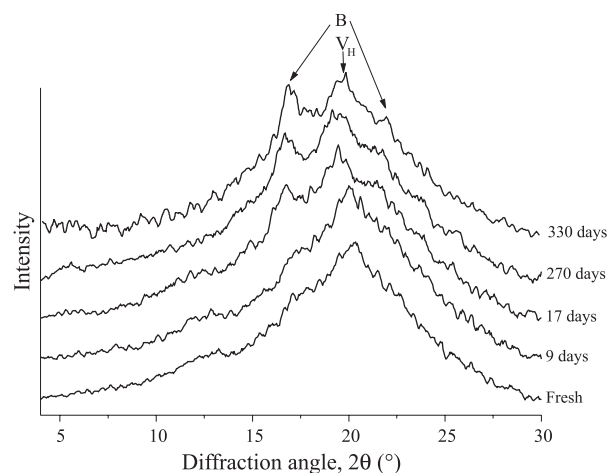


Figure 1. X-Ray diffractograms of plasticized cornstarch film as a function of aging time; (a) fresh film, after (b) 9 days, (c) 17 days, (d) 270 days and (e) 330 days.

films, 85 μm in average, the water content of the samples was equilibrated at 6% after 7 days. From the macroscopic point of view, there were no significant changes in the color of the films after 330 days.

Figure 1 shows the X-ray diffractograms obtained for plasticized cornstarch film stored at 50% RH over 330 days. The B- and V_H -type crystallinity indices were determined from these diffractograms and the results are presented in Table 1. A-type crystallinity of native cornstarch was not retained in cast starch films obtained by the experimental conditions used in this work.

Traces of B-type crystalline patterns indicated by a broad and small peak at $2\theta = 17^\circ$ ($X_{c,B-17^\circ}$) were detected in fresh films (films analyzed immediately after drying) (Figure 1). B-type crystallinity index of 0.060 in relation to $2\theta = 17^\circ$ ($X_{c,B-17^\circ}$) was measured for these films (Table 1). The short-term development of this type of crystallinity has been attributed to the fast re-crystallization of amylose molecules[6]. The main change observed in the diffractograms of Figure 1 was a gradual increase in B-type crystallinity. After conditioning for 17 days, starch films presented a clearly defined peak at $2\theta = 17^\circ$ and another B-type characteristic peak, at $2\theta = 22^\circ$. The $X_{c,B-17^\circ}$ was almost twice the value

Table 1. Crystallinity indices determined for plasticized cornstarch films as a function of aging time^a

Aging time (days)	$X_{c,B-17^\circ}$ (a.u.)	$X_{c,B-22^\circ}$ (a.u.)	$X_{c,VH}$ (a.u.)
0	0.061	0.0065	0.22
9	0.084	0.069	0.24
17	0.14	0.10	0.22
270	0.28	0.14	0.22
330	0.28	0.13	0.24

a. B-type crystallinity index related to the peak at $2\theta = 17^\circ$ ($X_{c,B-17^\circ}$); B-type crystallinity index related to the peak at $2\theta = 22^\circ$ ($X_{c,B-22^\circ}$); V_H -type crystallinity index related to the peak at approximately $2\theta = 20^\circ$ ($X_{c,VH}$).

observed for the fresh films. After 270 days, $X_{c,B-17^\circ}$ tended to an equilibrium value of approximately 0.28.

In Figure 1 and Table 1, it can also be observed that there were relatively large amounts of V_h -type crystallinity (peak at $2\theta = 20^\circ$) in fresh films and that it remained almost constant during aging. The V_h -type crystallinity index was 0.23, in

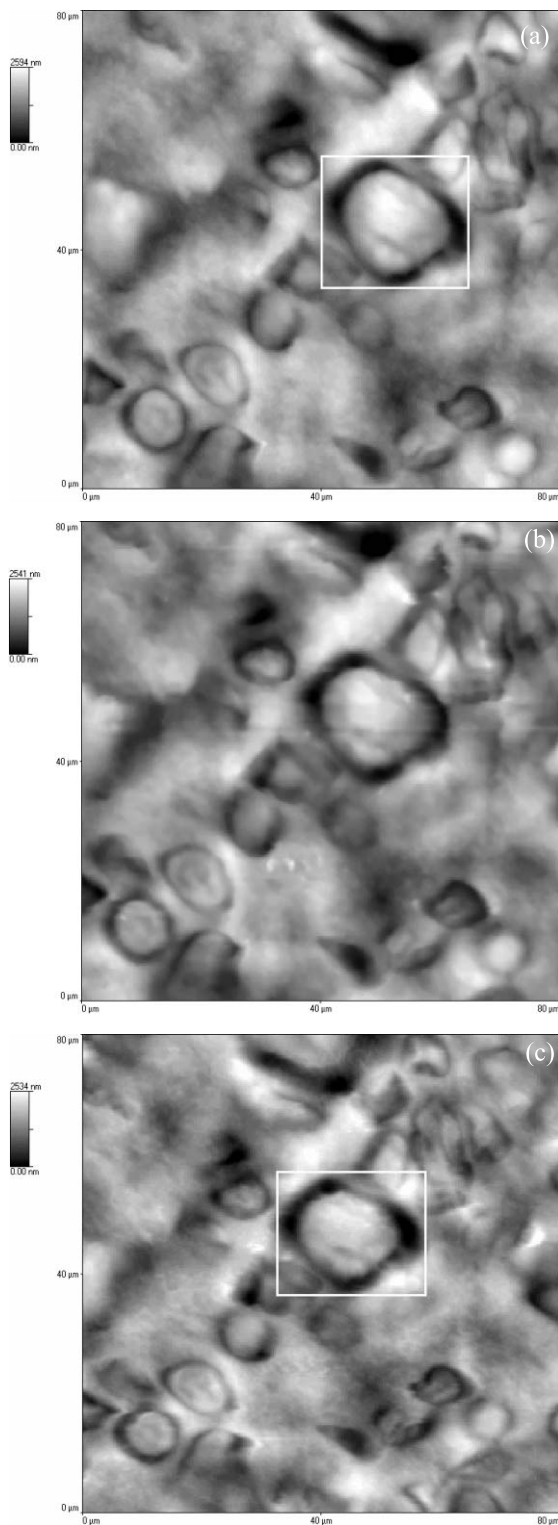


Figure 2. AFM topographic images of the same region of a cornstarch film conditioned at 50% RH for (a) 7 days, (b) 34 days and (c) 270 days.

average, over the 330 days of the experiments. This type of crystallinity is attributed to the precipitation of amylose-lipid complexes, which are formed after starch gelatinization. In the crystalline precipitate, amylose adopts a left-handed, single helical conformation^[9].

In a previous publication^[10], it was shown that the surface of partially gelatinized cornstarch films, obtained by casting, presented two distinct regions; a continuous region, called matrix and composed mostly of amylose molecules, and a granular region, which corresponded to slightly swollen starch granules, denoted granular envelopes. Figure 2 shows AFM topographic images of the same surface region of a cornstarch film exposed to 50% RH for 7 (a), 34 (b) and 270 days (c). It can be visualized that the general morphological aspect of the film was preserved, even after conditioning for 270 days. There was no significant change in the overall roughness of the region, which was determined as (448 ± 14) nm.

AFM allows accurate measurements of size and height of any features. The granular envelopes that are encircled by boxes in Figures 2a and 2c are detailed in Figures 3a and 3b, respectively. The topographical profiles of the line traced on the images are also shown. It can be observed that there were no significant changes in the dimensions of the granular envelopes after 270 days of aging. According to the profiles, this specific substructure presented in average (19.3 ± 0.4) μm in horizontal axis and (1819 ± 166) nm in height. Similar results were obtained for different granular envelopes. Although reorganization of amylopectin, a much slower process, influences the long-term behavior of starch systems^[11], this type of reorganization process (amylopectin retrogradation) was not detected on the surface of granular envelopes.

AFM phase contrast images at higher magnification were obtained for the matrix of films conditioned at 50% relative humidity for 7 (Figure 4a) and 270 days (Figure 4b). These images revealed that the matrices of the films are composed of well-defined oval and elongated features, independently of aging time. The matrix of a 270-day-old film (Figure 4b) presents a higher number of ordered features. This observation gives an indication that the ordered domains visualized in

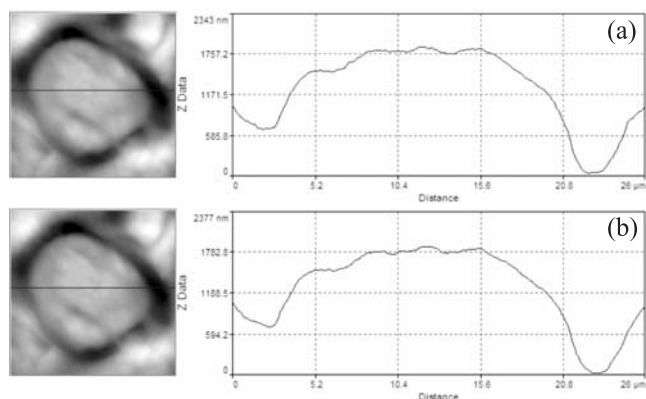


Figure 3. AFM topographic images of a granular envelope of a cornstarch film conditioned at 50% RH for (a) 7 days and (c) 270 days and the topographic profiles of the lines traced on the image.

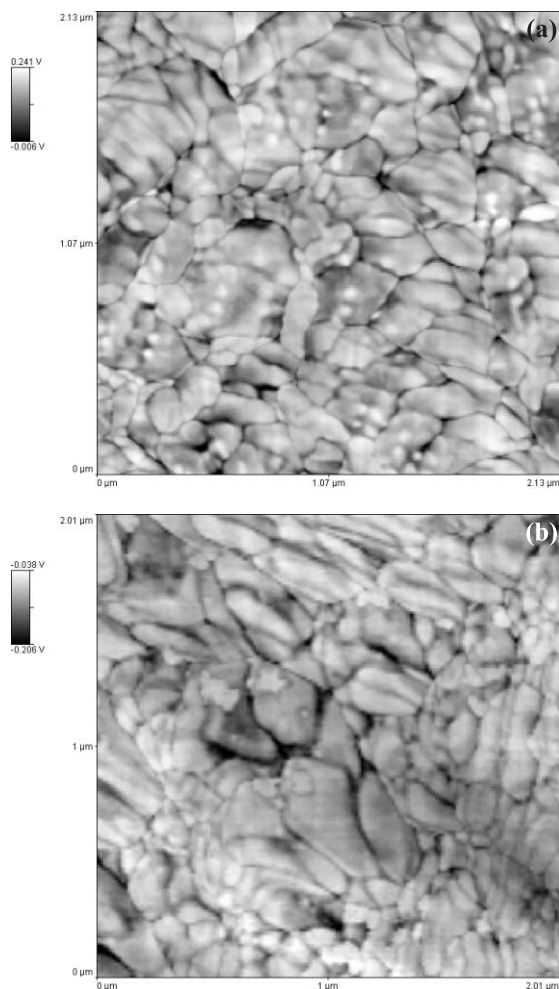


Figure 4. AFM phase contrast images of the matrix of a cornstarch film conditioned at 50% RH for (a) 7 days and (b) 270 days.

the matrix are related to the B-type crystallinity detected by X-ray diffraction (Figure 1).

An increase in the extension of water-glycerol phase separation due to the migration of the plasticizer to the surface during aging has been reported for thermoplastic oat and barley starch films^[12]. However, this phenomenon was not observed in the present study for cornstarch films.

Conclusion

The results of the present work corroborated that the crystallinity degree of cornstarch films varies considerably as a function of aging time. However, after conditioning for 270 days, the B-type crystallinity index tended to an equilibrium value. Although B-type crystallinity has been

correlated with amylose and amylopectin retrogradation, atomic force micrographs revealed no morphological changes at least at the surface of granular envelopes, which are known to be enriched in amylopectin. Nevertheless, slightly larger and ordered structures were observed at the matrix surface with aging, which is certainly linked to amylose retrogradation. It can be inferred that if retrogradation of amylopectin causes any changes in morphology of starch films, these changes might be present in the bulk of the films.

Acknowledgements

The authors thank F.T.G. Dias for experimental assistance and NUCAT/COPPE/UFRJ for permission to use the X-ray diffractometer. Financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Fundação Universitária José Bonifácio (FUJB) is gratefully acknowledged.

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