Investigation of the Surface Morphology of Plasticized Cornstarch Films

R.M.S.M. Thiré[1]; R.A. Simão[1] and C.T. Andrade[2]
[1]*Programa de Engenharia Metalúrgica e de Materiais, COPPE-UFRJ, PO Box 68505, 21945-970, Rio de Janeiro, RJ, Brazil; e-mail: rossana@metalmat.ufrj.br*
[2]*Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, PO Box 68525, 21945-970, Rio de Janeiro, RJ, Brazil*

Abstract

Atomic force microscopy (AFM) and optical microscopy (OM) were used to investigate the surface morphology of cornstarch films. The films were obtained by casting with glycerol and water as plasticizers. Similar morphologies were observed by OM and AFM operating in intermittent contact mode. Features of different shapes and sizes were visualized and attributed to swollen and partially disrupted granules. AFM phase contrast images revealed distinct structures occurring inside, outside and in the interface of the partially disrupted granules. This result was discussed in terms of phase separation.

Keywords: Cornstarch; Film formation; Phase separation; Atomic Force Microscopy.

Introduction

There has been much interest recently in the utilization of thermoplastic starch (TPS) for single-use biodegradable plastic items such as trash bags, shopping bags, dinner utensils, planting pots and diapers [5].

Starch is a complex homopolymer of α-D-glucose units consisting of two major types of polysaccharides - amylose and amylopectin. Amylose is mostly linear, whilst amylopectin is highly branched [2]. Native starch occurs as easily isolatable semycristalline granules. Amylose and the branching points of amylopectin form the amorphous regions in the starch granules. Amylopectin is predominantly responsible for granule crystallinity.

In order to be able to process native starch to form a bioplastic material, it is necessary to disrupt and melt the semicrystalline granular structure of native starches. Water and glycerol are the most commonly used plasticizers in TPS materials [7]. When heated in the presence of excess water, granular starch undergoes an order-disorder phase transition called gelatinization over a temperature range characteristic of the starch source [3]. Depending on processing and storage conditions, such as temperature and relative humidity, the amorphous starch undergoes structural changes after cooling, including amylose and amylopectin recrystallization into several crystal structures, phase separation and reorientation of polymers. The molecular interactions (mainly hydrogen bonding between starch chains) that occur after cooling have been called retrogradation. These interactions are found to be time and temperature dependent [8].

In this paper, AFM and optical microscopy (OM) were used to investigate the surface morphology of plasticized cornstarch films prepared by casting.

Materials and Methods

Food grade cornstarch was supplied by Refinações de Milho Brasil Ltda (São Paulo, Brazil). Cornstarch was dispersed in distilled water at 100°C (5% w/v) and kept under stirring for 5 min. Glycerol (15% w/w) was added as plasticizer. The hot dispersion was poured onto a Petri dish and allowed to dry at 50°C for 12 h. The films were peeled off and reconditioned for at least 2 days at 50% relative humidity before measurements. The thickness of the films was measured with a digital micrometer (Mitutoyo n° 293-265, Mitutoyo Corp., Japan). The films were 70-100 μm thick.

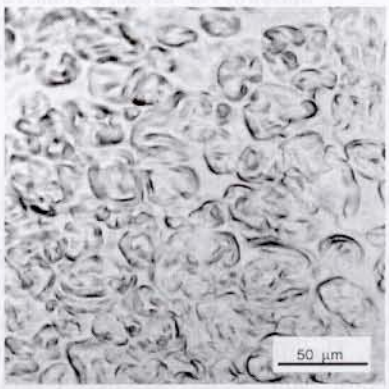
A Topometrix Accurex II (Topometrix, Santa Clara, USA) instrument, equipped with a non-contact AFM probe head and a 100 μm Tripot scanner was used to image the samples. The tips (Topometrix 1660TM) were made of Si and mounted on a cantilever with a spring constant of ca. 40 N/m and resonance frequencies in 100-150 kHz. 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 microscopy was operating in intermittent contact mode. Samples were fixed on double-coated adhesive tapes and the AFM images were obtained in air.

An Olympus BX60M optical microscope (Olympus America Inc, New York, USA) was employed to image the samples.

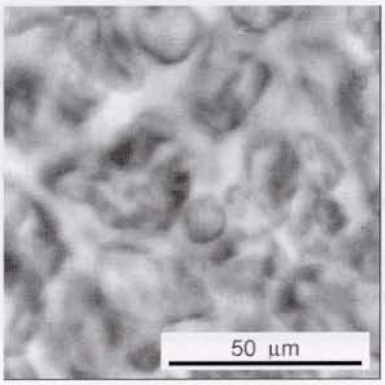
Results and Discussion

Films of cornstarch plasticized with water and glycerol were clear, homogenous and easily released from Petri dishes. Fig. 1a shows OM micrographs of a typical region of a plasticized cornstarch film surface. The image revealed that the surface consists of a homogenous matrix which contains irregularly spaced features with varied shapes and sizes. The same films were imaged by AFM in intermittent contact mode. Irregularly shaped features, similar to those observed by OM, may be observed in the topography image (Fig. 1b). This similarity confirms that AFM is a reliable technique to investigate the surface of bioplastic materials made of cornstarch.

Van Soest [9] suggested that the starch structure and morphology in thermoplastic starch (TPS) are determined by the level of disruption and melting of the granular starches and by the aging process. In excess of water, gelatinization is a two-stage process. In the first stage, the amorphous background region of the granules starts to take up water and to swell dramatically. The second stage is reached when this swelling process causes the disruption of crystallinity (uncoiling and dissociation of double helices) within the crystalline lamellae and ultimate breakdown of the granule [4]. Accordingly, the previous images show that the temperature and the stress conditions used in these experiments were not efficient enough to attain the critical level of water required in the amorphous background region for the complete rupture of the granules. Thus, it can be supposed that the surface features imaged should consist of swollen and partially disrupted granular starch, due to temperature and/or shear stress conditions, not efficient enough to attain complete gelatinization. As the amylose molecules are preferentially solubilized by water and are released from the granules in the initial stages of the gelatinization process [4], it seems reasonable to assume that the swollen granules are enriched in amylopectin, while the inter-granular space (matrix) correspond to a network structure made mostly of amylose. It is important to stress that the dimensions and shapes of the surface features are in good agreement with the scanning electron micrograph of cornstarch granules from the same commercial source used in the present work [6]. It was also observed (results not shown) that stirring the cornstarch dispersion for longer than 5 minutes provide the breakdown of the granules resulting in films with more homogenous surface.



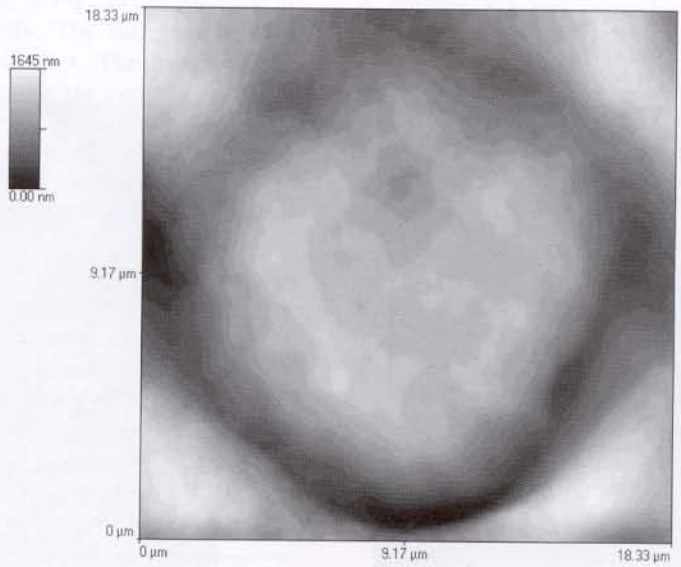
(a)



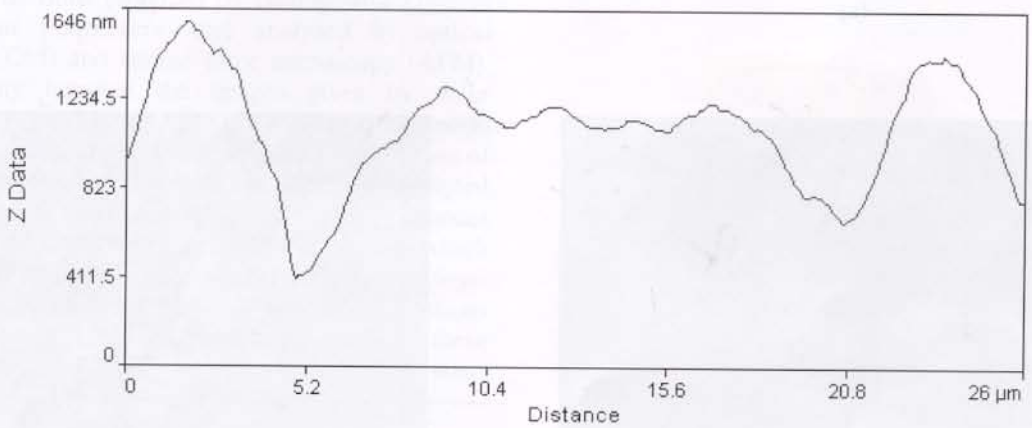
(b)

Fig. 1: (a) OM micrograph of cornstarch film surface. (b) AFM topographic image of the same film. Z height difference of 3.3 μm. For both images, scale bar = 50 μm.

Fig. 2 shows AFM images of a single granular feature with higher magnification. The topographic image (Fig. 2a) revealed a semispherical shape with approximately 15 μm in diameter and 0.8 μm in height, as shown in cross-section graphic in Fig. 2b. According to this Figure, the interface between the swollen granule and the surrounding matrix is depressed in height. As already observed in Fig. 1a, the lateral dimensions - size and shape - of the different features vary substantially but their general height aspect is the same as that presented in Fig. 2. Due to the high corrugation of the surface, morphological fine details can not be observed in topographic images.



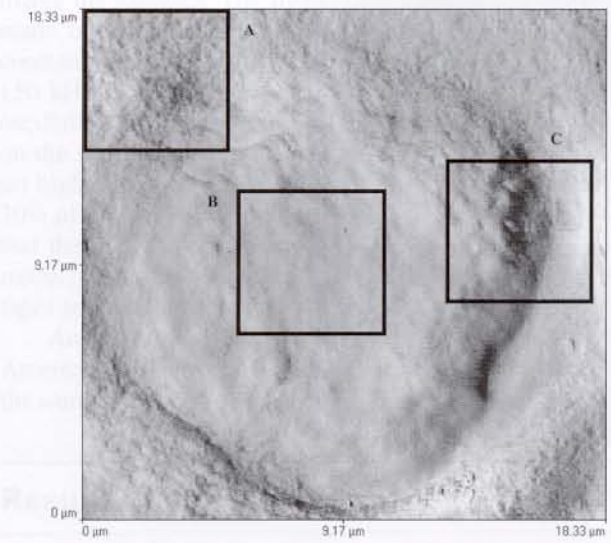
(a)



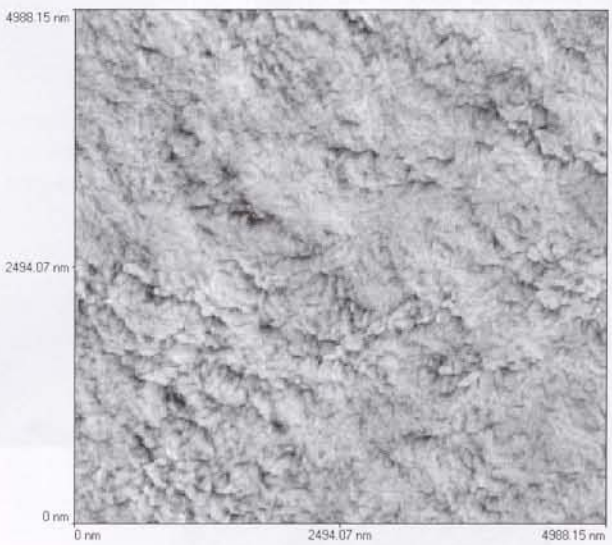
(b)

Fig.2: (a) AFM topographic image of a single granular feature of the surface of cornstarch film. (b) Diagonal cross-section of the feature.

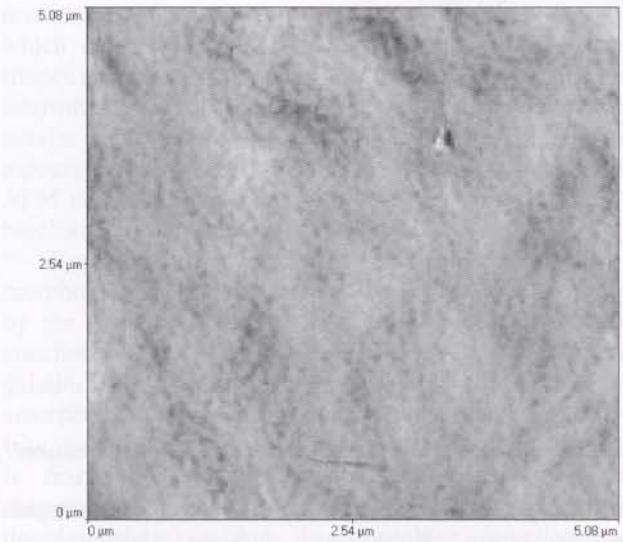
A phase contrast image of the same feature is shown in Fig. 3a and details of the region imaged is presented in Figures 3b-3d. The phase contrast image helps to distinguish the morphological surface differences between matrix, granular features, as well as the interface region between them. Parameters, such as elasticity and viscoelasticity, surface chemistry and instrumental parameters, besides morphological features, contribute to the phase contrast in AFM [1].



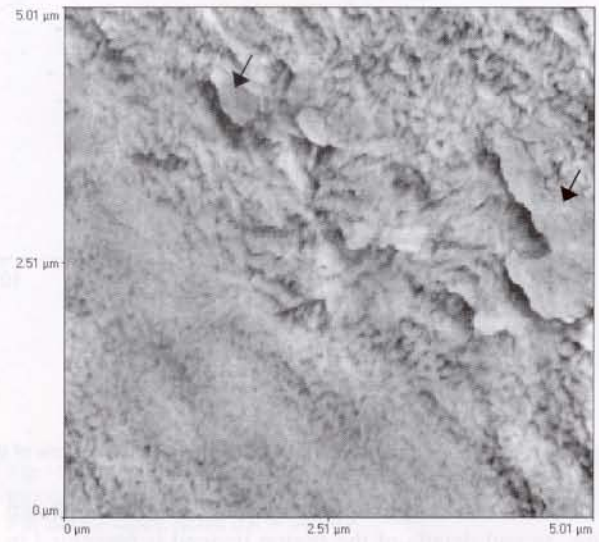
(a)



(b)



(c)



(d)

Fig. 3: (a) AFM phase micrographs of the same region imaged in Fig. 3 with 5 x 5 μm^2 images of details of different areas indicated by full-line boxes: (b) matrix (Box A); (c) internal region of feature (Box B) and (c) interface between matrix and feature (Box C).

Boxes A, B and C indicated in Fig. 3a are enlarged in Fig. 3b, 3c and 3d, respectively. The different regions exhibited characteristic morphologies. The image of the matrix (Fig. 3b) presents a significant contrast, while a surface with low contrast may be observed in the center of the granular feature (Fig. 3c). The image of the interface region between the swollen granule and the matrix (Fig. 3d) reveals a mixture of both morphologies presented in Fig. 3b and 3c.

Yuryev and co-works [10] demonstrated that the miscibility of amylose and amylopectin is generally limited. Consequently, the areas observed in the center of the granular feature and those indicated by the arrows in Fig. 3d may be related to the amylopectin-rich phase, since they present similar low phase contrast. Contrarily, the high contrast regions observed in the matrix and in the interface may be attributed to the amylose-rich phase.

Conclusion

Cornstarch films produced by casting with glycerol and water as plasticizers were analyzed by optical microscopy (OM) and atomic force microscopy (AFM). The similarity between the images given by these techniques assures that the AFM is a reliable technique to image starch films. The results showed that the surface of the films consisted of swollen and partially disrupted granules. Images provided by AFM phase contrast revealed fine details of different regions of the film, which was attributed to phase separation between the amylose-rich and amylopectin-rich phases. Further investigations have to be performed in order to confirm these assumptions.

Acknowledgments

We would like to thank the Brazilian agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FAPERJ (Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro) for financial support.

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