

## Development of Biodegradable Films from the Apple Bagasse for Controlled Release of NPK Fertilizer

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### ABSTRACT

*In recent years, the growing concern with environmental issues has been driving the development of new technologies as biodegradable films. These materials are made from natural polymers such as polysaccharides, proteins, and lipids. They are an interesting choice to meet the growing demand for products that do not cause harm to nature. In view of the above, this work aims at developing biodegradable films from the apple bagasse, which is a waste from juice production. The films applied to the controlled release of NPK fertilizer. The degradability of the films in the soil and the efficient controlled release of nutrients necessary for the development of plants are highlighted as the main results of this work.*

### Keywords

Apple bagasse, Biodegradable films, NPK fertilizer.

### Introduction

Fruit juice industries play an important part in the Brazilian agro-industrial sector, Brazil being one of the largest juice producers in the world.

Waste generation is one of the major problems that this sector faces. The amount of agro-industrial waste produced in southern Brazil, mainly by the juice and beverage industry, ranges from 30 to 40% (w/w) of waste per 100 t [1]. In order to reduce the impact on the environment, and to make use of the citric pectin obtained from the apple bagasse, this work aims at the production of biodegradable films using the apple juice waste as raw material.

The apple bagasse from the northeastern region of Rio Grande do Sul – Brazil has a high pectin content: from about 4 to 7% of pectin on a dry basis [2-4]. Pectin is a complex heterogeneous

polysaccharide, soluble in water, biodegradable and edible. It is widely used as a gelling agent and as a stabilizer in the food industry. It can be used to produce biodegradable films in which NPK fertilizer was incorporated. These films can then be used around plant seedlings for the controlled release of fertilizers.

Biodegradable films are prepared using at least two components: a matrix based on a biomacromolecule, which is capable of forming a cohesive structure, and a solvent [5]. Water is the most common solvent used to produce pectin films. A plasticizer such as polyvinyl alcohol (PVA) is used in order to improve the mechanical properties of the films, reducing brittleness and increasing flexibility, by changing the way in which the polymer chains interact with each other [6].

The main disadvantage related to polysaccharide films is their high hydrophilic. Crosslinking agents, such as oxalic acid or citric acid, are used to make the film less hydrophilic.

In agriculture, plastic materials have been used to build greenhouses, to pack seedlings, or to contain plants in nurseries, among other applications [7]. Despite all of these advantages, one can note the environmental impact caused by their use and inappropriate disposal. Biodegradable films are an alternative to the use of synthetic materials.

The purpose of this work is to evaluate the biodegradability of the apple bagasse film and its application in the controlled release of NPK fertilizer for plants such as cabbage.

## Materials and Methods

### Films production

The main raw material used for the film production was the apple bagasse (Gala and Fuji varieties) donated by Naturasuc Indústria e Comércio Ltda., Farroupilha – RS). Polyvinyl alcohol (PVA) (85,300 Da, 86.5-89.5% hydrolyzed) (Vetec) was used as a plasticizer and oxalic acid (Vetec) was used to promote gelation and cross-linking. The films were dried in a Teflon coated circular tray with diameter 24cm.

Different formulations were tested by varying the amount of oxalic acid as presented in Table 1.

Formulation	Apple Bagasse (g)	Polyvinyl Alcohol (g)	Oxalic Acid (g)
F1	40	20	5
F2	40	20	10
F3	40	20	15

**Table 1:** Raw material amounts used for the production of apple bagasse films.

The films were produced by casting method. First, 2 g of the previously crushed NPK 10-10-10 (%) (N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O) fertilizer (0.25 mm granulate), were solubilized in 200 mL of water. Then, the polyvinyl alcohol and the oxalic acid were dissolved at a constant temperature (70°C) for 5 hours. Finally, the previously crushed apple bagasse was added so that the crosslinking process could happen during a period of 3 hours at a constant temperature. Aliquots of the film-forming solution were casted onto Teflon plates. The solution was subjected to gelation and drying at 23°C for 24 h.

### Film characterization

#### Visual aspects and thickness

The visual aspects characterization was performed by subjective means, considering aspects such as homogeneity, polymer matrix continuity, easiness of detachment from the support and handling.

Some conditions applied during production can alter the film thickness. Pectin, for instance, when added to the process of production, has a film thinning effect, since it promotes a more compact molecular arrangement, which is commonly associated with the pectin's smaller molecular mass [9]. Thickness was obtained from the mean value of ten measurements taken different points of the film with a digital micrometer (Mitutoyo, 0-25 mm).

### Contact angle

From to determine the wettability of the material based on its contact angle with water. Angles greater than 90° indicate that the liquid does not tend to wet the surface and the material is said to be hydrophobic. For angles smaller than 90° the liquid is considered capable of wetting the material surface, so the material is hydrophilic. When the angle is equal to zero, complete wetness is obtained. Therefore, the smaller the contact angle obtained, the better the wetting [10].

For the determination of the contact angle of the apple bagasse film with water, samples were attached to a glass slide, in an environment with temperature set at 25 ± 2°C and relative humidity 60 ± 5 %. By means of a syringe, a drop of distilled water was placed on three different locations on the sample surface and the image of the drop was registered by a digital photographic camera to be analyzed with SurfTens software.

### Scanning Electron Microscopy (SEM)

The microscopic characterization of the films is important when a better understanding of their behavior is desired. SEM is a technique that can provide information capable of indicating structural and chemical properties of samples, such as imperfections and pore presence. Films can be evaluated according to their surface and the internal structure of the material when the cross section of the film, exposed by cutting, so it is analyzed in the electronic microscope [11]. Film morphology was evaluated by field emission gun scanning electron microscopy (FEG-SEM), TESCAN® brand, Mira3 model. The sample was dried in a greenhouse at 60°C for 24 hours. The dried sample was metalized with a thin gold layer and positioned on a carbon ribbon [12].

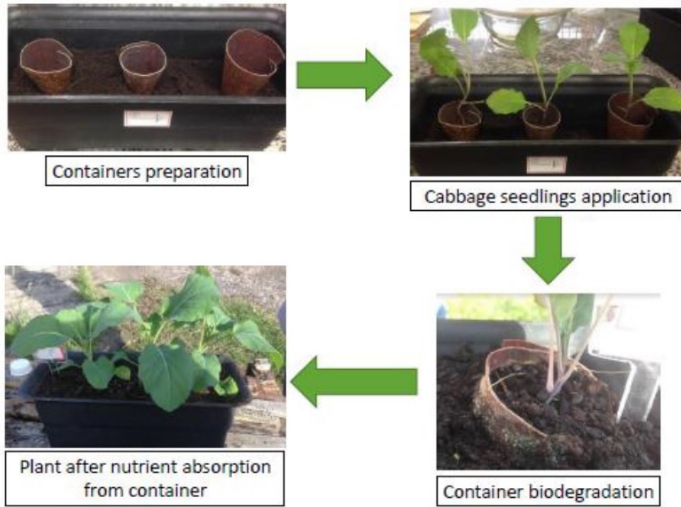
### Mechanical properties

Mechanical properties can define the application of polymeric films are affected by the film structure different factors, like plasticizer use, crystallinity and deformation percentage [13].

Thus, the mechanical properties of the apple bagasse films, such as tensile strength, were determined with a universal testing equipment EMIC brand, DL 2000 model from ASTM D882-10 norm (adapted) [14]. Seven samples of each sample prepared with 70 x 20 mm where tested. Deformation percentage (%) is the ratio between the length of the test sample at fracture and its initial length, that is, before being submitted to tension.

### Controlled release test

For the test of controlled release of nutrients, the apple bagasse film (0.5 mm of thickness), shaped as cones and immobilized with NPK fertilizer, was directly applied around the root of the cabbage seedlings, as shown in Figure 1. After 28 days of cultivation with temperature, humidity and luminosity control, the plants were harvested, washed and dried in an oven at an average temperature of 30°C. Observing the visual aspect of the plant it is possible to determine the average size of the roots and leaves. The degradability of the cones in contact with the soil was observed for 60 days.



**Figure 1:** Nutrients controlled-release tests performed with F2 apple bagasse films.

For the characterization of the fungi colonies present in the medium, scrapings of the fungi colonies growing on the films surfaces 30 days after tests were collected. Samples were examined, after lactophenol application, in a light microscope with 10x and 40x magnifications. With a wire loop, parts of the fungi colonies were inoculated into tubes containing sabouraud dextrose agar and incubated at 25°C for a week. For growth and identification of species and genre, the same procedure was performed to the dirt used in the biodegradation test.

## Results and Discussion

### Characterization of the films

**Visual aspects and thickness:** The F2 formulation produced a film with better aspects: continuous (no cracks), homogeneous (non-brittle), handy (capable of being handled and removed from the drying mold without breaking).

The table 2 shows the thickness of the apple bagasse films for F1, F2 and F3 formulations.

Formulation	Thickness (mm)
F1	0.430 ± 0.01
F2	0.451 ± 0.09
F3	0,472 ± 0,06

**Table 2:** Apple bagasse film thickness.

### Contact angle

Contact angle measurements were carried out on the surfaces of the films prepared by different formulations. After the water was applied to three different locations on the surface of each sample, five images were taken of each sample at time intervals of 30 minutes and the mean contact angle for each drop was calculated. The contact angles and the images of the drops on the surface of the films are presented in the table 3.

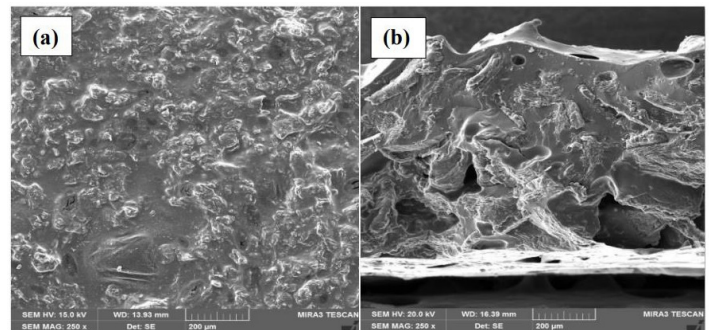
Sample	Contact angle with water after 10 minutes	Contact angle with water after 30 minutes	Images of the water drop after 30 minutes
F1	87.87° ± 0.8°	51.89° ± 1.2°	
F2	87.20° ± 1.2°	64.11° ± 0.8°	
F3	100.75° ± 0.5°	71.51° ± 1.5°	

**Table 3:** Contact angle between water and apple bagasse films of different thicknesses.

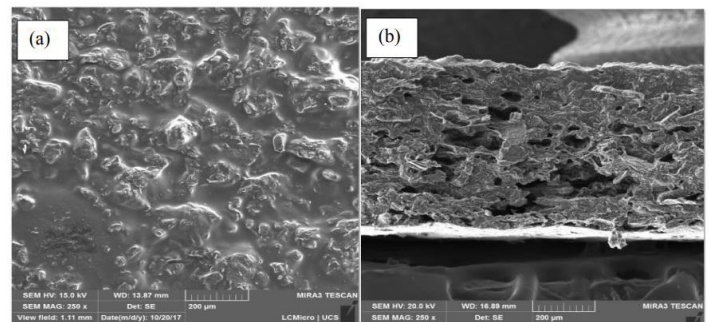
Despite the increase in the contact angle has provided by the higher concentration of oxalic acid on the formulation of the films, 30 minutes after the water was drop onto the films, all of them presented a contact angle smaller than 90°. Thus, these films can be considered hydrophilic.

### Scanning electron microscopy

Micrographs of the surfaces and cross sections of the apple bagasse films are presented in the Figures 2, 3 and 4. In Figures 2 and 3 irregularities and deformations can be seen on the surfaces of films F1 and F2. These films have a non-homogeneous, non-smooth surface. On the cross section, the films exhibited irregularities and small cavities.

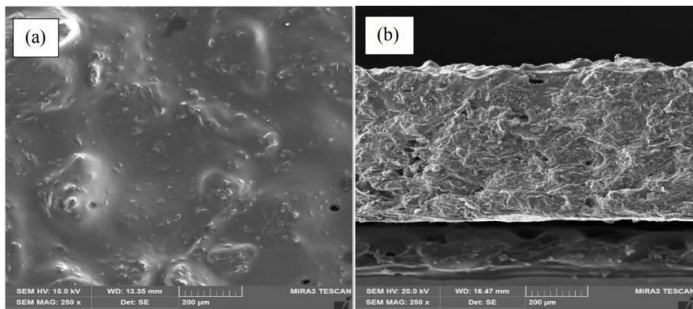


**Figure 2:** Micrograph (FEG-SEM) of the apple bagasse film for F1 formulation (a) surface (b) cross section (250x).



**Figure 3:** Micrograph (FEG-SEM) of the apple bagasse film for F2 formulation (a) surface (b) cross section (250x).

Figure 4 corresponds to the F3 formulation, a different morphology can be observed. The surface features less irregularities and remain uniform, smooth aspect on the whole analyzed area.



**Figure 4:** Micrograph (FEG-SEM) of the apple bagasse film for F3 formulation (a) film surface (b) cross section (250x).

Comparing all the micrographs (Figures 2, 3 e 4), the films had their properties improved with the increase on the amount of oxalic acid used on the formulations, which favored the processes of gelling and the interactions between ester and methyl groups, making them more uniform [15].

### Mechanical properties

Table 4 is presented the tensile strength (MPa) and elongation at break (%) results obtained for the all the formulations of apple bagasse films.

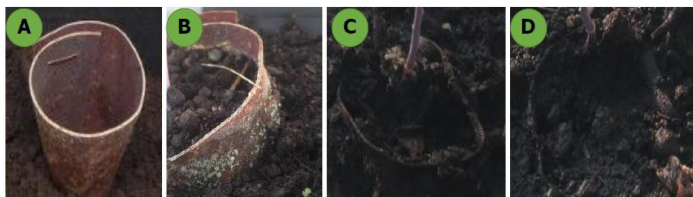
Formulation	Tensile strength (MPa)	Elongation (%)
F1	2.92 ± 1.6	30.84 ± 5.7
F2	2.96 ± 0.7	37.9 ± 10.3
F3	3.13 ± 1.2	46.3 ± 3.5

**Table 4:** Tensile strength and deformation of the apple bagasse films.

The best results were observed on the F3 films. The tensile strength was 3.13 ± 1.2 MPa and the elongation was 46.3 ± 3.5%. Due to the film morphology, observed on Figure 4, it can be verified that the increase in the concentration of oxalic acid result in more homogeneous and dense films. Even, the F3 films exhibited higher thickness. According to Sobral et al. (1999) [16], the properties of the films prepared by the technique of casting depend on their formulation, the kind and concentration of plasticizer used and the process of bonding between carbonic chains.

### Controlled release test

The results of the biodegradation test for the apple bagasse films (formulation F2) are shown in Figure 5.



**Figure 5:** Degradation of apple bagasse films (F2 formulation): (a) prior to the beginning of the degradation process, (b) 30 days, (c) 45 days and (d) 60 days after.

It is possible to observe the degradation of the films over the course of the days by the action of microorganisms present in the soil such as the fungus *Trichoderma sp.*, found in the films 30 days after the beginning of the tests. Fungus contributed to the almost complete degradation of the films in 60 days. A small amount of soil mixed with water was tested to identify the presence of bacteria, protozoa, spores, worms and colonies of gray filamentous fungi of *Rhizopus spp.*

According to Kolybaba et al. (2008) [17] the microorganisms present the environment can easily digest biodegradable materials in a period between 6 and 12 weeks, generating carbon dioxide, water and biomass as products, leaving no toxic waste.

### Conclusion

The biodegradable films of apple bagasse presented different characteristics depending on the concentrations of oxalic acid which favors gelation and crosslinking. The films with immobilized NPK fertilizer presented the ability of controlled release of the nutrient. They also degraded in contact with the soil, where the action of moisture, microorganisms and environmental characteristics were determinant factors. Films with high solubility be interesting when used in products that require hydration prior to use, such as agricultural seed that require rapid germination. This new container can be an alternative to the current polymer packages, in which it is not possible to add the nutrients necessary for the plants' development. This possibility arises from the fact that this polymer is produced with an agro-industrial waste that can be biodegraded by several types of microorganisms in the soil.

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