

## **Preparation and biodegradation analysis of starch films reinforced with coconut bagasse cellulose (*Cocos nucifera* L.)**

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### **Abstract**

Plastics have been developed as materials with specific characteristics to market demands (durable, cheap and light). However, those for single use are a worldwide success due to their low or no degradation. The objective of this work was to obtain biodegradable films from biopolymers and determine their biodegradation time in soil. Three formulations were made: starch and glycerol (Control), starch, cellulose 0.05%, glycerol (A1) and starch, cellulose 0.1%, glycerol (B1). The thermal capacity and percentage of crystallinity were determined by differential scanning calorimetry (DSC). Mechanical tests were obtained using a Texturometer. Its biodegradation capacity was determined by weight loss in soil and characterization by scanning electron microscopy (SEM). Sample B1 presented the best mechanical and thermal characteristics with a fracture stress of 15.07 MPa, an elongation of 18.025%, Young's modulus of 30.428 MPa and a melting temperature of 136.16 °C. The biodegradation time of the materials added with cellulose had an average of 20 to 25 days, A1 and B1, respectively. Obtaining biodegradable materials from starch and reinforced with cellulose from coconut residues, can contribute to the mitigation of the production and excessive use of single-use materials.

**Keywords:** biopolymers, agricultural residuals, mechanical characteristics

## **1. INTRODUCTION**

The human being is challenged by a wide range of environmental pollutants. The efforts and demands to try to combat the serious problem of environmental pollution caused by non-biodegradable plastic materials, have fostered the search for new alternatives, including the use of macromolecules that behave similarly to synthetic polymers. As reported by García et al [1], Vanin et al. [2], Avena-Bustillos et al. [3] and Alanís-López et al. [4], the use of natural macromolecules (starch, cellulose, pectins, chitin, chitosan, among others), is a good alternative in obtaining plastic packaging materials.

A wide range of natural polymers obtained from renewable resources, are being used to obtain materials with a biodegradable nature [5]. Some, such as cellulose and starch are increasingly used in the search for alternatives, while others are still underused. The development of biodegradable films is carried out in order to replace plastics derived from petroleum; due to the composition of its polymeric matrix these can be incorporated into the environment [6].

In general, films made with starch have shown good barrier behavior to gases and aromas [4]. On the other hand, the mechanical properties that present has been one of the main challenges to combat since it has limited its use [3]. Cellulose has characteristics of rigidity, resistance, hydrophilicity, compatibility, stereoregularity, biodegradability, stability and chemical capacity, and if there is a good homogeneous dispersion of cellulose particles in a polymeric matrix, good mechanical and performance properties are obtained from the composite material [7]. From elsewhere, the ease of chemical modification of the cellulose surface makes it an ideal candidate for its use as a reinforcer of materials with a biodegradable nature.

For that reason, the objective of this work was to produce starch films reinforced with cellulose and determine their degree of biodegradation in soil, in order to propose alternative materials that help mitigate the excessive use of petroleum derivatives.

## **2. MATERIAL AND METHODS**

The cellulose was extracted from coconut bagasse through a chemical and thermal process. The jicama starch was donated by the Technological Development Laboratory of the CEPROBI-IPN, Mexico.

### **2.1 Casting method**

For the production of biodegradable films, the Mali method [8] was used. The starch was hydrated with distilled water for 30 min and subsequently it was subjected to heating to 45 °C with constant stirring. Cellulose and glycerol were added, the solution was left at 60 °C for 30 min; a filmogenic solution was obtained, which was poured into a Petri dish. Finally, it was dried at 40 °C for twelve hours. The film was stored at 25 °C ± 2 °C in a desiccator, with a relative humidity (RH) of 57%, with a saturated NaBr solution.

## 2.2 Thermal analysis

Thermal properties were determined using the methodology proposed by Sobral et al. [9]. A differential scanning calorimeter (TA, 2010 New Castle) was used for the analysis. The equipment was calibrated with Indium (melting point 156.4 °C and an enthalpy of 28.47 J/g), calibrating with the liquid nitrogen baseline as a cooling medium, heated from -100 °C to 130 °C at a heating rate of 10 °C/min. The sample was subjected to a heating program two consecutive times in a temperature range of -150 °C to 130 °C and a heating rate of 10 °C/min generating an inert atmosphere in the cell, by circulating 45 mL/min, of nitrogen gas (purity 99%). Glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and enthalpy of fusion ( $\Delta H$ ) were obtained from the test.

### 2.2.1 Crystallinity

The degree of crystallinity was determined based on the DSC enthalpy of fusion data using the equation 1 [10]:

$$X_c = \frac{\Delta H_f}{\Delta H_o} \quad (1)$$

Where  $X_c$  is the crystalline fraction,  $\Delta H_f$  represents the enthalpy of fusion measured by DSC and  $\Delta H_o$  is the enthalpy of fusion for 100% crystalline polymer.

## 2.3 Mechanical properties

The mechanical properties of the films were determined using a TAXT2i texturing equipment (Stable Micro Systems™, Surrey, UK), equipped with a 25 Kg load cell. The films were studied following the ASTM method D-882-02 [11]. The tensile strength (TS), elongation (%E) and Young's modulus were determined using a deformation rate of 1 mm/s. Samples of each formulation were cut (100 mm long by 10 mm wide) for analysis. The films are kept for 7 days in desiccators with a saturated saline solution of NaBr, 57% RH.

## 2.4 Biodegradation of films in soil

For the biodegradation test, the samples were cut (3 cm<sup>2</sup>) and placed on the surface of the Petri dish which contained the soil mixture. The weight loss evaluation was determined gravimetrically, using a balance. The films were weighed before and after the biodegradation study and in this way, a record was created in a spreadsheet to process the results obtained and determine the percentage of weight loss, after 5, 10, 15, 20, 25 and 30 days of biodegradation. Once the samples are extracted, the excess soil is removed, they were washed with distilled water, until any trace of soil was removed. They were dried for 2 hours at 60 °C and subsequently weighed. The calculation of the loss in weight was using the equation 2:

$$\% \text{ weight loss} = \frac{\text{starting weight} - \text{final weight}}{\text{starting weight}} \times 100 \quad (2)$$

A photographic follow-up and an analysis by scanning electron microscopy were also carried out, to obtain a characterization of the surface of the films during the biodegradation process.

### 2.5 Scanning Electron Microscopy (SEM)

The samples were placed on a double-adherent carbon conductive tape, fixed on the aluminum support of the Carl Zeiss EVO LS 10 scanning electron microscope. The samples were observed at a voltage of 2.5 kV, with a resolution of 3-10 nm; the micrographs were taken at various magnifications [12].

## 3. RESULTS AND DISCUSSION

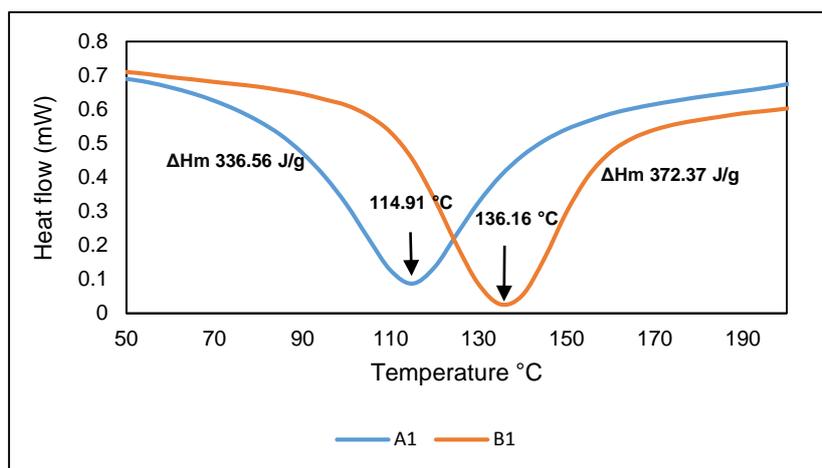
Control films based on jicama starch-glycerol and jicama starch reinforced with cellulose to 0.05% and 0.1% coconut bagasse and glycerol were obtained (Figure 1). The appearance of samples A1 and B1 was grainy, not smooth and with the naked eye you can see a faint yellow color while the control film was transparent. This perhaps due to the presence of some cellulose particles.



**Figure 1.** Biofilms: (a) control sample, (b) A1 sample and (c) B1 sample.

### 3.1 Thermal analysis

In Figure 2 you can see the thermogram of the film A1 and B1, where the peaks of melting temperatures ( $T_m$ ) and enthalpy of melting ( $\Delta H_m$ ) are presented.  $T_m$  is related to a significant movement of molecular chains due to alteration of the crystals as the temperature increases [13].



**Figure 2.** Thermal transition of films from starch/cellulose 0.05 % (A1) and starch/cellulose 0.1 % (B1).

Adding cellulose to the polymer matrix increased the enthalpy and temperature of the composite films; the values were higher for B1 (temperature of 136.16 °C and  $\Delta H_m$  372.37 J/g). Results are similar to those found in mango fibrous endocarp cellulose and starch films reported by Lorenzo-Santiago *et al.* [14], where the melting temperatures increase when adding cellulose to the polymeric matrix and go from 76.92 to 128.65 °C and the  $\Delta H$  from 4.61 to 236.43 J/g.

According to what was reported by Kaushik *et al.* [15], the behavior of films with cellulose increases their  $\Delta H$ , indicating that biofilms reinforced with this biopolymer improve their ability to resist high temperatures.

### 3.1.1 Crystallinity

The control sample presented a crystallinity of 31.52%. When adding cellulose, the crystallinity of the film increased its percentage to 41.59 and 42.81 for formulation A1 and B1, respectively (Table 1). These findings indicate that the cellulose interfered with the crystalline arrangement of the starch structure, thus causing an increase that were observed in the percentage of crystallinity in A1 and B1 films.

**Table 1.** Percentage of crystallinity of the films (% Xcc).

Sample	% Xcc
Control	31.52
A1	47.59
B1	54.81

This behavior may be due to a stabilizing effect on the interaction of cellulose fiber with amylose [16]. The higher the crystallinity, the better thermal stability and fracture properties the material can acquire.

### 3.2 Mechanical properties

The results obtained for fracture stress (TF), percentage of elongation (%E) and Young's modulus are reported in Table 2. The control film presented the lowest values in all the mechanical properties, while in cellulose reinforced films their mechanical characteristics increased considerably. The interaction between cellulose and starch determines the mechanical properties, in terms of tension and elongation [17].

**Table 2.** Mechanical properties of films.

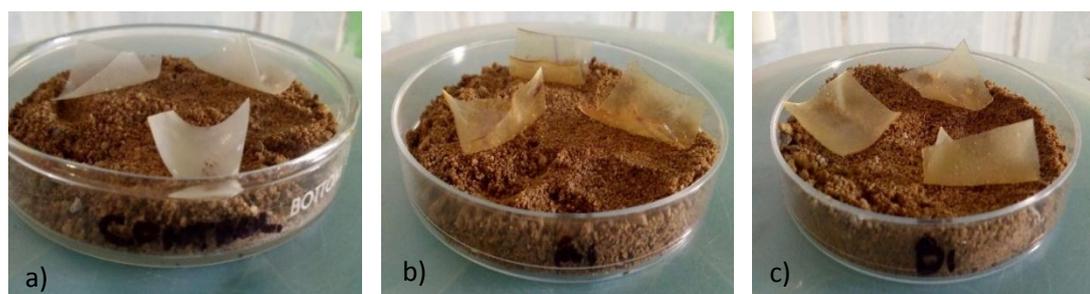
Sample	Fracture stress (MPa)	% Elongation	Young's modulus (MPa)
Control	8.337	4.499	4.0321
A1	10.453	15.650	15.853
B1	15.078	18.025	30.428

The addition of cellulose at 0.05% and 0.1% considerably increased the tensile strength and Young's modulus. This is due to the increasing number of bonds that are formed with the starch, thus increasing the stiffness of the film. Similarly, the percentage of elongation increases with the addition of cellulose in the polymeric matrix. The reinforced films present values higher than those reported by Jannah et al. [18] in films added with rice husk cellulose and chitosan, where they report a stress at fracture of 0.03 MPa and 9.93% elongation. The values found are similar to those reported by Chen et al. [19], in films made with thermoplastic starch added with crystalline cellulose, reporting a stress at fracture of 4.48-6.61 MPa and an elongation percentage of 30%.

Because the matrix and charges have similar chemical properties, good affinity is expected to form strong bonds in composite films, which is reflected in presenting a favorable reinforcement effect [20].

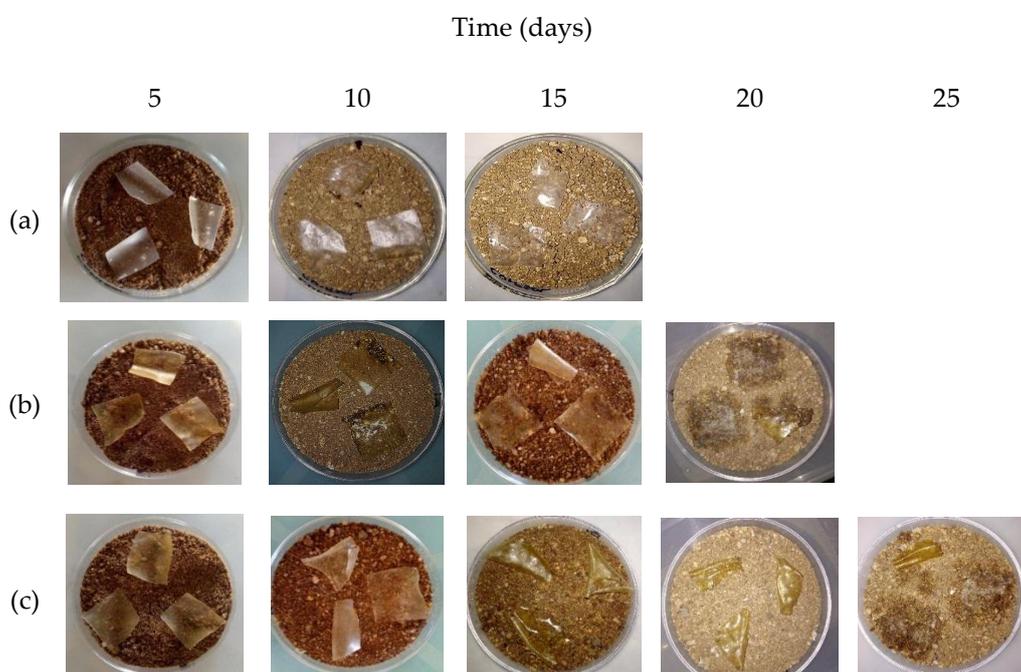
### 3.3 Biodegradation of films in soil

Figure 3 shows the control, A1 and B1 samples at the beginning of the biodegradation test with exposure to soil. Being in contact with the soil, it is more feasible for microorganisms to find carbon sources and start to metabolize them, generating the weight loss of biofilms [21].



**Figure 3.** Films subjected to biodegradation studies: (a) control, (b) A1 and (c) B1 at time zero.

At five days of development of the test, pores and small white spots are observed on the surface of the control film; whereas, cellulose-reinforced starch samples show no changes in color or appearance (Figure 4).



**Figure 4.** Photographs of samples under laboratory conditions to observe biodegradation of film samples: (a) Control, (b) A1 and (c) B1.

The changes observed in the films after ten days in soil, are attributed to the concentration of starch and glycerol used in the formulation of the materials. The control film has larger pores on its surface, its white coloration turned to a more subdued transparent (Figure 4).

Film A1 presents the edges with a dark brown coloration, for this biodegradation time

the attack of microorganisms in this formulation can already be observed. Due to the hydrophilic nature of the polymeric matrix, it favors the absorption and increase in water activity, promoting the growth of microorganisms. In film B1 the first pores appear in the center of the material, indicating the presence of microorganisms and the start of biodegradation for this formulation.

After 15 days of contact with the soil, the control film exhibits the most pronounced signs of biodegradation with the presence of pores on the entire surface (Figure 4), the color change is evident and a significant mass loss. Sample A1 begins to disintegrate and dark spots can be seen on the surface, action awarded to the leaching of glycerol. The B1 film begins to absorb moisture and its consistency is soft with pores on its entire surface.

20 days after the experiment the control film has completely disintegrated, preventing the percentage of weight loss from being taken. A1 film exhibits an advanced degree of biodegradation and two of the three samples in the petri dish have completely degraded. The three B1 film samples in the petri dish have suffered a deformation, the probable causes are attributed to the absorption of water and the polymeric matrix [22].

25 days after exposure to the soil the A1 film has completely disintegrated, only the weight of a B1 film sample could be determined and which presented cracks and fractures (Figure 4). The attack of the microorganisms was very evident on the surface. For the 30 days of exposure of the samples on the soil the B1 film broke into small pieces as a result of the biodegradation process therefore, the recovery of the fragments was not possible, to evaluate the loss in weight.

As reported by Gama [23], in cellulose-reinforced gelatin films with 0.05%, 0.01% and 0.15%, the biodegradation of materials with these polymeric matrices, it happened at 25 days with a weight loss of 75, 78 and 80%, respectively. These values are similar to those found in this biodegradability test.

The determination of the degradation of the films in soil evaluated the biodegradable behavior of the mixtures added with cellulose under simulated conditions. Applying the Equation 2 the percentage of biodegradation was calculated and the data is presented in the table 3.

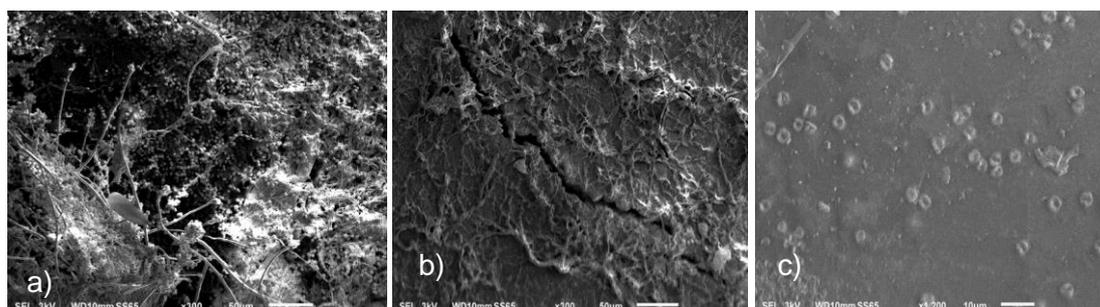
**Table 3.** Percentage of biodegradation calculated with equation 2.

Sample	Biodegradation test time (days)					
	5	10	15	20	25	30
Control	63.87	71.36	83.03	-	-	-
A1	13.29	32.36	72.44	82.85	-	-
B1	10.95	28.00	64.34	73.73	83.65	-

The control film was degraded after 15 days of exposure in soil with a loss of 83.03% in weight. Sample A1 presented a weight loss of 82.85% at 20 days and B1 presented a loss of 83.65% and its maximum degradation time was 25 days.

### 3.4 Scanning Electron Microscopy (SEM)

An analysis of the surface of the biofilms was carried out after 15 days of exposure in soil in order to characterize the three formulations, this because the control film was degraded in that time. The control film exhibited the highest biodegradation and is completely fractionated. The micrograph shows the presence of fungal spores and mycelia invading the surface (Figure 5). Being composed only of starch and glycerol, it is more attractive as a carbon source for microorganisms.



**Figure 5.** Micrographs of (a) Control, (b) A1 and (c) B1 samples.

The surface of the A1 film is cracked. Likewise, mycelia covering the surface and large pores could be observed. On the other hand, film B1 has small pores on the surface. The degradation by microorganisms is not so evident yet, action that is awarded to the fact that it has a higher percentage of cellulose in the matrix, causing a slower assimilation by microorganisms.

The pores and fractures present on the surface in the A1 and B1 films are similar to those reported by Astilleros [24], in a film composed of sorghum starch, cellulose and glycerol and which were degraded in 30 days. The deterioration of the material is the result of the activity of microorganisms growing on the surface and inside [25,26].

Microorganisms and environmental factors such as: humidity and temperature, cause the physical and chemical changes reflected to the naked eye, in addition to intervening in the porosity of the materials.

## CONCLUSION

The elaboration of the formulations of the film was suitably carried out by the pour-plate method, technique commonly used at the laboratory which made it possible to obtain films of considerable thickness and easy detachment for further characterization. Film A1 had a melting temperature of 114.91 °C. However, B1 showed better thermal capacity, with a melting temperature of 136.16 °C and an enthalpy of 372.37 J/g. The crystallinity of the A1 and B1 films increased by 16.07% and 23.29% compared to the control film. The B1 films presented the best percentages of elongation, fracture stress and Young's modulus. The biodegradation test showed a control film that was degraded

at 15 days, losing 83.5% weight. The film added with 0.05% cellulose lost 82.85% at 20 days of biodegradation and the 0.1% fiber reinforced film was degraded on day 25, registering a loss of 83.65% in weight. The use and exploitation of coconut bagasse, will allow the waste generated not to be considered as materials that do not have any commercial value. On the contrary, the use of coconut residues in obtaining biodegradable materials could be established as a possible solution to the problem of environmental pollution caused by non-biodegradable plastic materials.

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### CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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