



Biodegradability and mechanical properties of starch films from Andean crops

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ABSTRACT

Different Andean crops were used to obtain starches not previously reported in literature as raw material for the production of biodegradable polymers. The twelve starches obtained were used to prepare biodegradable films by casting. Water and glycerol were used as plasticizers. The mechanical properties of the starch based films were assessed by means of tensile tests. Compost tests and FTIR tests were carried out to assess biodegradability of films. The results show that the mechanical properties (UTS, Young's modulus and elongation at break) of starch based films strongly depend on the starch source used for their production. We found that all the starch films prepared biodegrade following a three stage process and that the weight loss rate of all the starch based films tested was higher than the weight loss rate of the cellulose film used as control.

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1. Introduction

Starch has been used as raw material for the production of biodegradable plastics due to its biodegradable properties, low price and abundant availability [1–10]. Thermoplastic starch (TPS) and polylactic acid (PLA) are by far the most important biodegradable plastic available in the market. Both use starch as raw material in their production [11].

Starch is the main energy reserve in higher plants [12]. It is accumulated in storage organs like tubers or seeds over long periods of time that allow the formation of large granular structures [12]. The most industrially important sources of starch are corn, wheat, cassava and potato starch. They are composed of two types of complex carbohydrate polymers of glucose, namely amylose (20–30%) and amylopectin (70–80%). Amylose is a linear polymer of glucose units linked with α -1,4-bonds. Amylopectin, which is an extremely high molecular weight polymer, has the same backbone structure of amylose, but with many α -1,6-linked branch points [2,13–16].

Starches from different sources differ in their amylose to amylopectin ratio showing different properties. When starch is heated in the presence of water, starch granules swell irreversibly and amylose leach into the aqueous phase. This phenomena associated with the disruption of granular structure by breaking of H-bonds is known as gelatinization. Starch gelatinization occurs at different temperatures depending on the type of starch. Generally, the gelatinization process takes place at around 70 °C under atmospheric pressure [14,17–19].

Starch is not truly a thermoplastic, but in the presence of a plasticizer at high temperature and under shear, it can melt and flow. Thus, it can be extruded or injected, similarly to thermoplastic polymers [20]. Water and glycerol are widely used as plasticizers since they have a low molecular weight and glass transition temperature. The processing techniques, processing conditions and the use of plasticizers have an important impact on the final properties of the starch based materials [19,21–25].

The tensile strength of starch films decreases with the addition of plasticizers. Lourdin et al. [26] have compared the mechanical properties of glycerol plasticized starch films and pure starch films. Pure starch films have tensile strength values of around 45 MPa while glycerol containing starch films have tensile strength values of around 10 MPa.

In addition, the structure and properties of biodegradable materials change due to exposure to air, soil microorganisms, and UV radiation [27]. Mechanical properties of starch based products are also affected by these factors. The biodegradability of starch based products can be evaluated using composting tests. During composting tests a biological decomposition process takes place under controlled aerobic conditions [28]. This biological decomposition is accomplished by living organisms (e.g., bacteria and fungi). These organisms determine the rate of composting since they have enzymes that permit them to degrade solid wastes.

Andean ecosystems offer different varieties of native Andean crops which represent a potential source of different types of starch. This paper discusses the suitability of these starches biodegradable plastics. The aim of the present work is to report the mechanical properties of starch films prepared from different varieties of Andean crops, and also to investigate the biodegradation behavior of such films.

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Table 1
Andean crops used for the production of starch based films.

Code	Common name	Part	Scientific designation
WCA01	White carrot	Vegetable root	<i>Arracacia xanthorrhiza</i>
CHI01	Chickpea	Legume	<i>Cicer arietinum</i>
BAN01	Banana	Fruit	<i>Musa paradisiaca</i>
OCA01	Oca	Tuber	<i>Oxalis tuberosa</i>
CAS01	Cassava	Tuber	<i>Manihot esculenta</i>
SPO01	Sweet potato	Tuber	<i>Ipomoea batatas</i>
POT01	Gold potato	Tuber	<i>Solanum goniocalyx</i>
POT02	'Huamantanga' potato	Tuber	<i>Solanum tuberosum</i>
POT03	'Mariva' potato	Tuber	<i>Solanum tuberosum</i>
POT04	'Muru-huayro' potato	Tuber	<i>Solanum tuberosum</i>
POT05	'Peruanita' potato	Tuber	<i>Solanum tuberosum</i>
POT06	'Yungay' potato	Tuber	<i>Solanum tuberosum</i>

2. Materials and methods

2.1. Preparation of starch films

Starch was extracted from twelve varieties of native Andean crops. Starch sources are listed in Table 1. Plant parts containing starch were cleaned with tap water and chopped. The chopped samples were homogenized in a blender, sieved and left for decantation. After 4 h, supernatant was discarded and precipitate was degreased by resuspension with 1:1 metanol:water mix and decanted again. The remaining starch precipitated at the bottom of the container. Finally, the obtained starch obtained was dried at 60 °C for 24 h.

Starch films were prepared by casting. Dried starch was diluted in distilled water to form a 5% (w/w) starch solution. This solution was partially hydrolyzed in dilute hydrochloric acid (0.1 N) adjusting pH to 2.0. Glycerol was added at ratio of 2:5 (glycerol:starch (dry basis)). The starch solution was homogenized by stirring for 15 min at 95 °C. Then, the solution was neutralized in dilute sodium hydroxide (0.1 N) adjusting the pH to 10 to stop hydrolysis. Finally, the starch solution (7% (w/w)) was spread on Petri dishes and placed in an oven at 40 °C. After 16 h of drying, films of about 200 µm in thickness were obtained.

2.2. Tensile properties

Mechanical properties of starch films were determined by tensile test. A bench top tensile testing machine (ESM Mark-10), equipped with a 10 N ($\pm 0.5\%$) load-cell, was used in the experiments. The crosshead speed was set at 10 mm/min. Samples were cut into strips of 5 mm \times 50 mm. Four samples were tested per starch type. These tests were performed at room temperature (15–20 °C). Young's modulus, ultimate tensile strength (UTS) and maximum strain were measured.

2.3. Biodegradation test of starch films

Organic compost was used to evaluate biodegradability of starch films. The moisture content of the compost was fixed to 50% to enable aerobic conditions. The pH of compost was fixed within a range of 7.0–8.0.

Starch films were cut into 25 mm \times 25 mm squares. Samples of around 150 mg were used. All samples were immersed in water and ethanol (96% purity) for 3 and 2 min, respectively. Then, they were dried at room temperature for 16 h. Dried samples were weighed for the first time. Finally, each sample was covered with a fine mesh and placed in an opaque polyethylene vessel containing around of 200 mg of compost. The incubation time was 31 days. Samples were weighed every day in order to evaluate the weight lost during biodegradation.

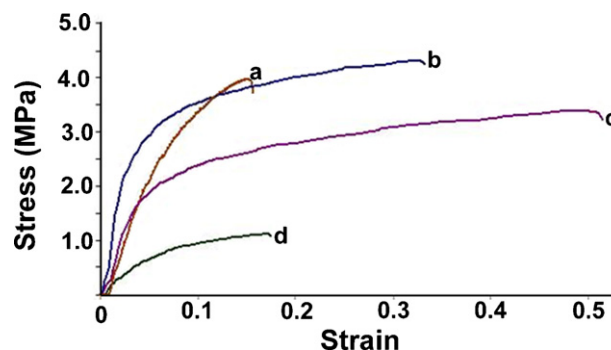


Fig. 1. Representative stress–strain curves of starch films obtained from (a) gold potato, (b) sweet potato, (c) cassava and (d) corn.

2.4. Fourier transformed infrared spectroscopy tests

Starch films were tested in order to evaluate the effect of biodegradation on the IR spectrum. Starch samples were washed with distilled water, then ground and dried in a desiccator overnight. IR analysis of samples in KBr was performed in a Gangdong FTIR-7600 Series, FTIR.

3. Results and discussions

3.1. Mechanical properties of starch films

Starch films were prepared from twelve varieties of Andean crops (Table 1). A fixed glycerol concentration of 40% was used to prepare starch films. Mechanical properties of such films are depicted in Table 2. Films prepared from cassava and sweet potato starch, had the highest values of elongation at break, 43% and 33%, respectively. Table 2 shows that the value of elongation at break of starch films increases as their UTS values decrease.

As shown in Fig. 1, mechanical properties of starch films depend on the starch source. The representative curves (Fig. 1) show that starch films display an elastomeric behavior. This behavior is associated with the presence of glycerol on films. Due to this elastomeric behavior, Young's modulus was calculated from the initial linear region (up to 1% strain). The highest value of Young's modulus (E) was found for sweet potato starch based films (106 MPa) whereas the lowest value correspond to white carrot starch based films (15 MPa).

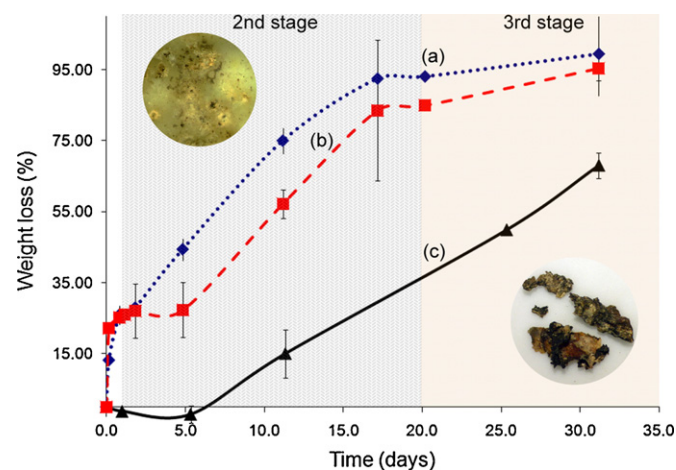


Fig. 2. Representative weight loss curves of a (a) cassava starch film, a (b) sweet potato starch film and a (c) cellulose film used as control. The three stages described on the text can be observed. Inserts show the external appearance of starch films at the end of the 2nd and 3rd stages.

Table 2

Mechanical properties of starch based films prepared from Andean crops.

Code	Samples	UTS (MPa)	Elongation at break (%)	Young's modulus (MPa)
WCA01	White carrot	1.99 ± 0.58	22.60 ± 4.95	15.00 ± 1.14
CHI01	Chickpea	4.14 ± 1.05	16.82 ± 2.23	50.38 ± 3.79
BAN01	Banana	5.01 ± 2.06	14.30 ± 1.28	46.86 ± 17.37
OCA01	Oca	5.91 ± 2.12	17.25 ± 3.43	54.86 ± 18.10
CAS01	Cassava	2.56 ± 0.73	43.45 ± 12.80	30.27 ± 12.05
SPO01	Sweet potato	3.72 ± 1.12	33.83 ± 9.11	106.01 ± 42.19
POT01	Gold potato	3.99 ± 0.67	18.05 ± 4.57	51.59 ± 1.48
POT02	'Huamantanga' potato	2.68 ± 0.48	21.90 ± 4.77	22.05 ± 1.74
POT03	'Mariva' potato	5.00 ± 1.05	17.20 ± 4.23	57.12 ± 1.84
POT04	'Muru-huayro' potato	4.77 ± 1.54	29.20 ± 5.19	41.46 ± 3.59
POT05	'Peruanita' potato	3.78 ± 1.03	22.64 ± 2.13	29.45 ± 1.84
POT06	'Yungay' potato	3.22 ± 0.34	24.18 ± 4.95	41.37 ± 7.93

Table 3

Weight loss of starch based films during compost test.

Code	Sample	% Weight loss during composting		
		1 day	15 days	30 days
WCA01	White carrot	28.01 ± 3.02	98.65 ± 1.23	99.20 ± 0.13
CHI01	Chickpea	27.61 ± 1.12	82.98 ± 7.36	91.36 ± 1.85
BAN01	Banana	27.43 ± 0.49	90.45 ± 3.83	95.98 ± 0.27
OCA01	Oca	24.6 ± 0.71	85.42 ± 2.67	98.26 ± 0.39
CAS01	Cassava	25.79 ± 1.73	93 ± 0.90	99.35 ± 0.00
SPO01	Sweet potato	25.96 ± 1.05	84.96 ± 4.54	95.38 ± 0.67
POT01	Gold potato	27.58 ± 2.63	84.48 ± 11.76	90.03 ± 1.41
POT02	'Huamantanga' potato	27.31 ± 0.40	96.31 ± 0.86	98.22 ± 0.30
POT03	'Mariva' potato	25.85 ± 0.74	91.43 ± 3.42	98.34 ± 0.26
POT04	'Muru-huayro' potato	26.89 ± 0.77	92.95 ± 0.84	97.01 ± 0.02
POT05	'Peruanita' potato	26.9 ± 2.14	88.18 ± 3.48	97.87 ± 0.02
POT06	'Yungay' potato	27.88 ± 0.22	86.11 ± 6.39	96.58 ± 1.69

The mechanical properties of the films depended on the type of starch used to prepare these films. Films made from banana starch are more brittle than the others. Films from cassava and sweet potato starch are both strong and tough. These films can absorb more energy than the others, since they undergo higher strains before breaking.

3.2. Biodegradability of starch films

The weight loss during degradation of starch and cellulose control films is shown in Table 3. The weight of the starch films decreased leading to a total weight loss of more than 90% after 31 days. The highest percentage of weight loss was observed for cassava starch-based films (99.35%), whereas the lowest percentage of weight loss was observed for gold potato starch-based film (90.03%). In contrast, the cellulose control films only lost around 30% of weight in the same period of time. This difference

is attributed to the fact that glycosidic alpha linkages in starch are more easily broken down than glycosidic beta linkages in cellulose.

All the starch films tested displayed a similar degradation behavior that can be represented in three stages (Fig. 2). In the initial stage, the samples achieved a weight loss of around 30% in the first 24 h. This first degradation mechanism is mainly associated with the leaching of glycerol.

Fig. 3 shows the IR spectra of a sweet potato starch film during different degradation times. The spectrum before composting shows a peak at 3307 cm⁻¹ which is related to hydroxyl groups present on starch–glycerol films [29,30]. It can be seen that after 24 h of composting, the intensity of such a peak decreases. This is in agreement with the observation of glycerol leaching during the first 24 h of composting and explains the high weight loss of the first degradation stage.

The second stage is in the order of 20 days. During this stage, the weight of starch films declined steadily, until 90% of the orig-

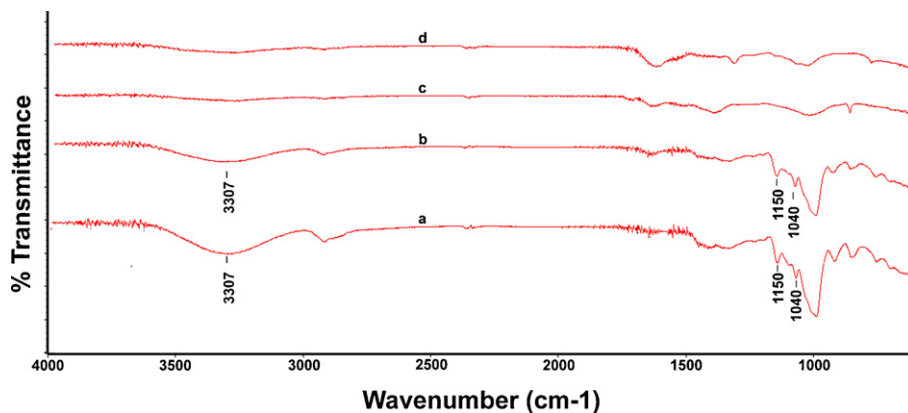


Fig. 3. Representative IR spectra of sweet potato films (a) before composting test and after (b) 24 h, (c) 11 days and (d) 21 days in compost.

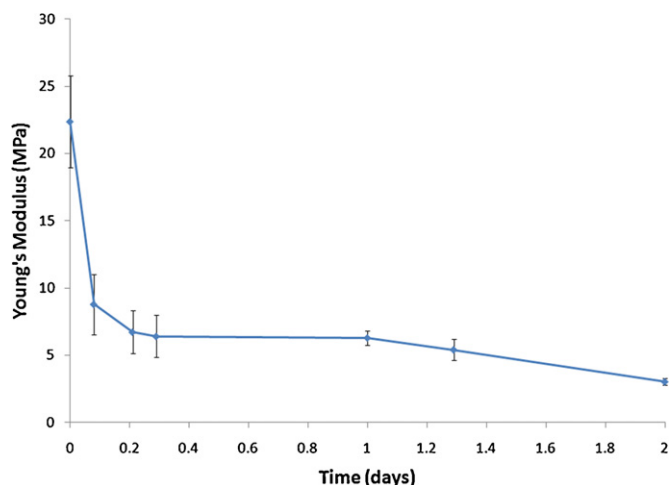


Fig. 4. Change in the values of Young's modulus of a sweet potato starch film as a result of composting process.

inal weight. This stage is characterized by a lower rate of weight loss. The degradation mechanism at this stage is associated with the biological activity present in the composting vessels. Such biological degradation can also be observed in the FTIR spectra. In fact, the intensity of the peaks associated with starch glycosidic linkages ($1150\text{--}1040\text{ cm}^{-1}$) decreased indicating the action of α -amylase [31].

The third stage has a duration of around 10 days. At the end of this stage, the weight loss of starch films was 95%. Although the rate of degradation decreased dramatically, the appearance changes are considerable. Starch films were broken into small species as a result of the degradation process (insert in Fig. 2).

As expected, the mechanical properties of starch films decreased due to biodegradation. Fig. 4 shows that the Young's modulus of sweet potato starch films decreases from 106 MPa down to 2 MPa, and then it remains constant.

4. Conclusions

We have used starches obtained from different Andean crops to produce biodegradable films by a casting method. The mechanical properties of films such as Young's modulus, UTS and elongation at break were dependent on the starch source used. Mechanical tests confirmed the loss of mechanical properties after degradation. The weight loss rate during the compost tests of all starch based films was higher than the weight loss rate of cellulose films used as control. The biodegradation process was found to have three stages characterized by the weight loss rate. FTIR tests confirmed that the first degradation stage was associated with glycerol leaching. This

paper shows that the Andean crops studied can be potentially used as raw material for the production of biodegradable polymers.

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