The utilization of coconut wastes for bioplastic production

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ABSTRACT

Plastics have been developed as materials with specific characteristics to market demands (durable, economical and light). However, single-use plastic waste is a worldwide event due to its low or no biodegradability. Pollution problems related to the disposal of solid waste associated with these polymers, both in the agricultural sector, companies and society in general, have generated the search for alternatives that help reduce the impact generated by these materials. The objective of this work was to take advantage of the coconut bagasse (*Cocos nucifera* L.) in obtaining natural polymers that allow the production of bioplastics. The microcellulose was characterized by scanning electron microscopy (SEM) and its thermal capacity and percentage of crystallinity were determined by Differential Scanning Calorimetry (DSC). The microcellulose was dispersed in starch/glycerol to obtain bioplastics as follows: control C or starch/glycerol with no microcellulose addition; A_1 or starch/glycerol and microcellulose at 0.05% and A_2 or starch/glycerol and microcellulose at 0.1%, respectively. The SEM of cellulose showed the removal of lignocellulosic walls, as well as fibers with diameters 40 and 400 µm. The native fiber presented an endotherm at 116.41°C and the microcellulose at 143.67°C. The bioplastics observed by SEM presented a surface with irregularities, it was grainy, not soft, and at first glance you could see some large particles associated with processing operations. Sample A_1 presented the best calorimetric characteristics. Obtaining bioplastics materials from coconut residues will help mitigate the production and excessive use of single-use materials.

Key word: Coconut waste; bioplastic;

INTRODUCTION

The efforts and demands to try to combat the serious problem of environmental pollution caused by non-biodegradable plastic materials, have led to the search for new alternatives in the use of macromolecules that behave similarly to synthetic polymers (García *et al*., 2004; Vanin *et al*,. 2005; Avena-Bustillos *et al*,. 2006). Natural polymers such as cellulose and starch obtained from renewable resources, they are being used to make biodegradable materials; although still many other agroindustrial resources such as coconut bagasse are still underutilized.

Coconut (Cocos nucifera L.), is widely distributed in islands and tropical coastal areas around the world, in Mexico it comprises 190,000 hectares destined for its production of about one million tons of coconut which yield about 166,000 tons of copra, that once processed give approximately

100,000 tons of oil (SAGARPA, 2019). 10% of the production is used as fruit and in the manufacture of sweetmeats, while 90% is dedicated to the copra from which 60-70% oil is extracted, of which 90% goes to the manufacture of soaps and only 10% related food. While cultivation is important from an economic point of view, there is a problem in the accumulation of coconut bagasse waste since before the few alternatives of recovery and use of bagasse, producers draw upon to burning or improperly dispose of this waste.

Coconut bagasse is a fibrous by-product from coconut and like others organic wastes have potential in producing non-biodegradable plastic materials, due to high complex saccharide in a form of lignocellulose (Lara *et al*., 2019). Use of agricultural fibres that come from agricultural wastes for product development (Reza *et al*., 2017), generates added value to coconut cultivation, and avoid that this ends up in open air dumps, that is incinerated, buried or used as fuel in the bakery and brick industry.

Starch is a polysaccharide of multiple industrial applications (Biliaderis, 1991; Larotonda *et al.*, 2004), it is isolated by physical means from various botanical sources, with corn being the most widely used industrially, followed by potatoes, wheat and rice (Myers *et al*., 2000). However, in recent years the search for unconventional alternative sources for its extraction and use, which allow obtaining new or better functional properties for product development (Mali and Grossman, 2003; Bourtoom and Chinnan, 2008). In addition to taking advantage of regional agricultural resources that are underutilized, like the jicama. This is why the objective was to take advantage of the coconut bagasse in obtaining natural polymers that allow the production of biodegradable plastics.

Material and Methods

The raw material that was used was: coconut bagasse and jicama starch. El Centro de Desarrollo de Productos Bioticos (CEPROBI-IPN), located in Yautepec, Morelos, Mexico provided the starch.

Bagasse sample preparation

The chemical modification of the coconut bagasse was followed by the method developed by Salgado-Delgado *et al*. (2010). The bagasse was cut into 1-2 cm long sections (fibres), washed with distilled water for 10 min with shaking, and dried in an oven at 60°C for 24 h. According to Morales *et al*. (2001) mercerization was performed; the fibres were moistened in 10 mL of a 40% NaOH solution, 90 mL of distilled water and 400 mL of methanol were added and kept stirring for 4 h. to finally do a wash with ethanol/water (50:50 v/v) and dried at 60°C for 24 h. Slight modifications were made to the acid hydrolysis methodology (Moran et. al., 2008) reducing the amount of H_2SO_4, as well as increasing temperature and stirring time. The fibres were treated with 200 mL of a 17.5% NaOH solution for 6 h to perform alkaline modification, neutralized using 1 N HCl, filtered and dried at 60°C for six hours. A solution of sodium hypochlorite/glacial acetic acid (4:2 v/v) was used to bleach the fibres, with some modifications as was increasing the amount of washings and the concentration of sodium hypochlorite/glacial acetic acid. The modified fibres were ground for later use.

Scanning electronic microscopy (SEM)

The morphology of the fibres and bioplastics from all samples was observed with a Philips XL30 SEM (Philips, Holland) and observed at a voltage of 20 kV. Using SEM, fibres and bioplastic was mounted on aluminium specimen holder by double-sided tape and micrographs from the surface (magnification 50, 500 and 600 X) were taken (Rendón-Villalobos, *et. al.*, 2010).

Thermal analysis

The thermal properties were studied using a differential scanning calorimeter (DSC) (TA Instrument DSC 2100 New Castle, DE). The calibration was done with Indium (point of fusion of 156.4°C; enthalpy of 6.8 J/g). The base line was achieved by running a heating program from 25 to 250°C; 7 to 8 mg of sample were placed on an aluminium pan. This pan was sealed and as reference an empty aluminium pan was used. The analysis was performed through a heating program over a temperature range from 20 to 220°C and a heating rate of 10°C min^{-1} with nitrogen flow rate of 40 mL min^{-1} (Quintanar *et al.*, 2009). The melting temperature (T_m) and transition enthalpy (ΔH, evaluated by integrating the peak area, corresponding to such transition), were obtained from the tests.

Crystallinity Index

The degree of crystallinity was performed based on the DSC enthalpy of fusion data using the following equation (Poley *et al.*, 2004):

$$X_c = \frac{\Delta H_f}{\Delta H_o} \tag{1}$$

Where X_c is the crystalline fraction, ΔH_f represents the enthalpy of fusion measured by DSC and ΔH_o is the enthalpy of fusion for 100% crystalline polymer.

Preparation of bioplastics

The method of Mali et al. (2002) was used for the preparation of bioplastics, an aqueous dispersion of jicama starch, cellulose and 4% glycerol (w/v) was prepared. Three formulations were made: control C (starch/glycerol) with no microcellulose, A_1 (starch/glycerol/ microcellulose at 0.05%) and A_2 (starch/glycerol/microcellulose at 0.1%). The starch was mixed with distilled water and maintained at 45°C with constant agitation for 30 min; cellulose and glycerol were added and kept at 60°C for 30 min. The filmogenic solution was poured into the glass molds, allowed to dry at 40°C in an oven for twelve hours to form the bioplastic. Once the bioplastic was formed, it came off carefully.

Results and Discussion

Extraction of coconut bagasse fibres

During the mercerization, sodium hydroxide reacted with the structure of lignin and hemicelluloses, generating rupture and subsequently removing them, thus leaving cellulose available in the medium. During acid hydrolysis the fibre size decreased considerably, on the other hand, this process helped eliminate impurities from mercerization.

Bagasse scanning electronic microscopy (SEM)

The native bagasse has very compact outer layers covering the cellulose sacs, lignin packs the cellulose on the outside of the fibre, providing its property of stiffness and hardness to the fibre (Samir *et al.*, 2004; Lorenzo-Santiago, 2016). The structure of the native bagasse showed a diameter of ~ 347 μm (Figure 1a), however, when the process of mercerization is carried out the impact of sodium hydroxide can be seen observing the release of hemicellulose and tannins whose function is to keep the structure of the fibres together (Figure 1b). The fibres are elongated and need an acid treatment to remove the lignin layers that hold together the cellulose sacs.

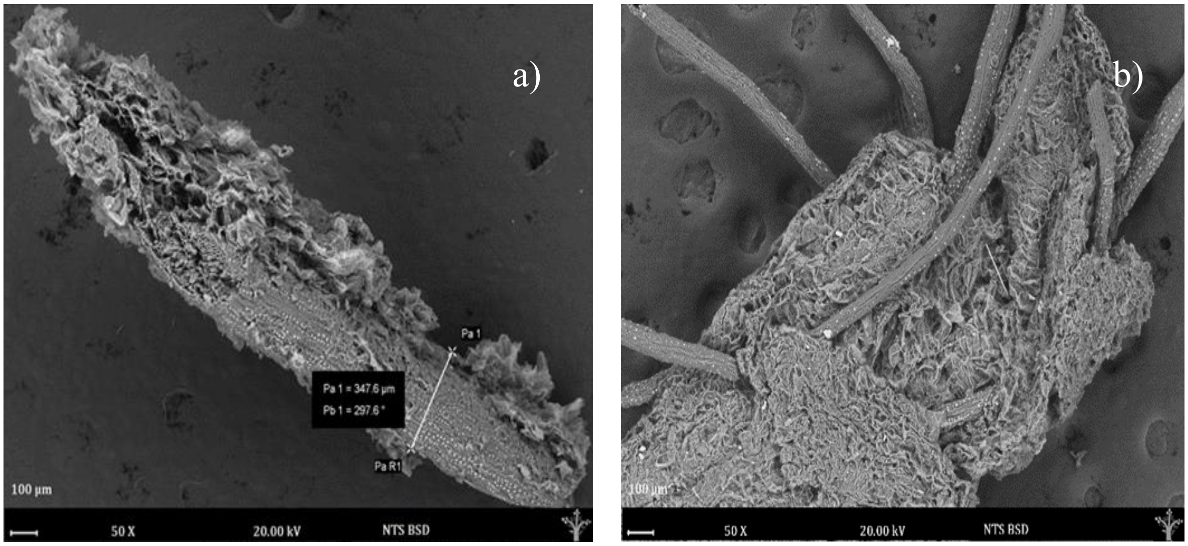

Figure 1. SEM micrographs of coconut bagasse: (a) native and (b) modified by acid hydrolysis.

As the bagasse is subjected to a series of alkaline modifications, it is observed how the separation of cellulosic filaments begins (Figure 2a). After alkaline modification and bleaching, individual fibrils can be seen that have separated from the sine of the cellulosic filaments and that show a decrease in thickness and size (Figure 2b), their sizes found range between 40 and 400 µm.
The removal of lignin due to chemical modifications has made cellulose fibres more available, which means that it can be mentioned that the objective was met.

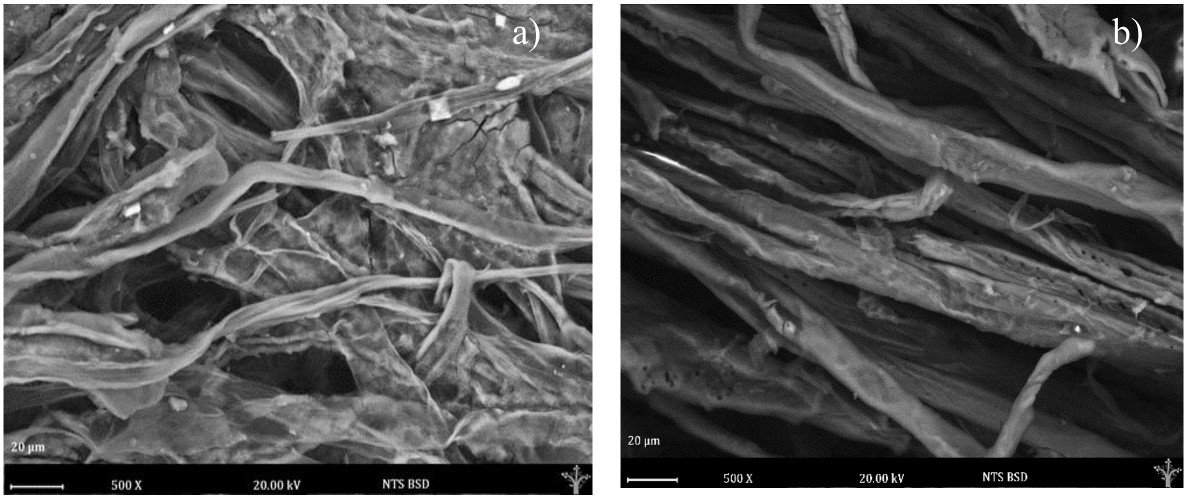

Figure 2. SEM micrographs of coconut bagasse with alkaline modification (a) and whitening (b).

Bagasse Thermal analysis and Crystallinity Index

Results of melting temperature (T_m) and transition enthalpy (ΔH) for native and modified samples are showed in Table 1. The T_m values for both samples increased from 116.41 to 143.67ºC indicates that, when the native fibres go through the process of modification tend to increase their heat capacity, this is attributed to the amount of cellulose.

The greater the amount of cellulose, the more energy it will take to degrade (Xiao *et al*., 2001; De Dios Naranjo *et al*., 2016). The increase of 27.26°C, may indicate a greater stability of the fibres once they pass a chemical process and, therefore, can provide greater thermal stability to the materials that use the microcellulose within their polymer matrix. The enthalpies of the endotherm were 135.98 J/g for native and 198.40 J/g for microcellulose, probably by the elimination of larger chains present in cellulose, therefore, more heat energy is used for degradation to occur.

Table 1: Thermal parameters and crystallinity index of coconut bagasse native and modified.

Fibre	T_m (°C)	ΔHm (J/g)	% Xcc
Native	116.41	135.98	74.71
Modified	143.67	198.40	80.91

It is widely recognized that cellulose contains a crystalline and an amorphous region (Klemm *et al*., 2005). The index of crystallinity in native fibre and microcellulose was calculated from the data obtained from thermal analysis (Table 1). According to Li et al. (2009), the percentage of crystallinity in native fibre will always be lower due to the presence of amorphous compounds (hemicellulose and lignin). On the other hand, the percentage of crystallinity is increased by the elimination of amorphous regions of cellulose, product of hydrolysis (Spagnol *et al*., 2012). Similar values of 82.83 and 83.57% of crystallinity have been reported by García-García et al. (2013) for a native bagasse of sugarcane and wood pulp. Other values of crystallinity in bagasse of Abacá, Jute and Lino (63, 64 and 63%), have been reported by Barba-Pacheco, (2002). The presence of amorphous regions in the fibres, allow better penetration of chemical reagents, therefore, greater reactivity. The greater the crystallinity of a fibre, the better thermal stability and properties it can provide in a poly mix to obtain biodegradable materials. This loss of amorphous areas, as in modified bagasse, confirms the removal of lignin (mainly amorphous) and with whitening the crystallinity of bagasse increases. The crystalline zones are responsible for the mechanical resistance and amorphous areas are associated with the flexibility and elasticity of the material, so these results are interesting since what is sought is to use cellulose fibres as reinforcement in biodegradable materials but that at the same time allow to use less chemical agents such as plasticizers.

Bioplastic scanning electronic microscopy (SEM)

The morphologies of the films were visualized superficially from micrographs at 600 X magnification. The control sample showed a surface with irregularities (Figure 3a), it was grainy, not soft, and at first glance you could see some particles associated with processing operations of the filmogenic solution.

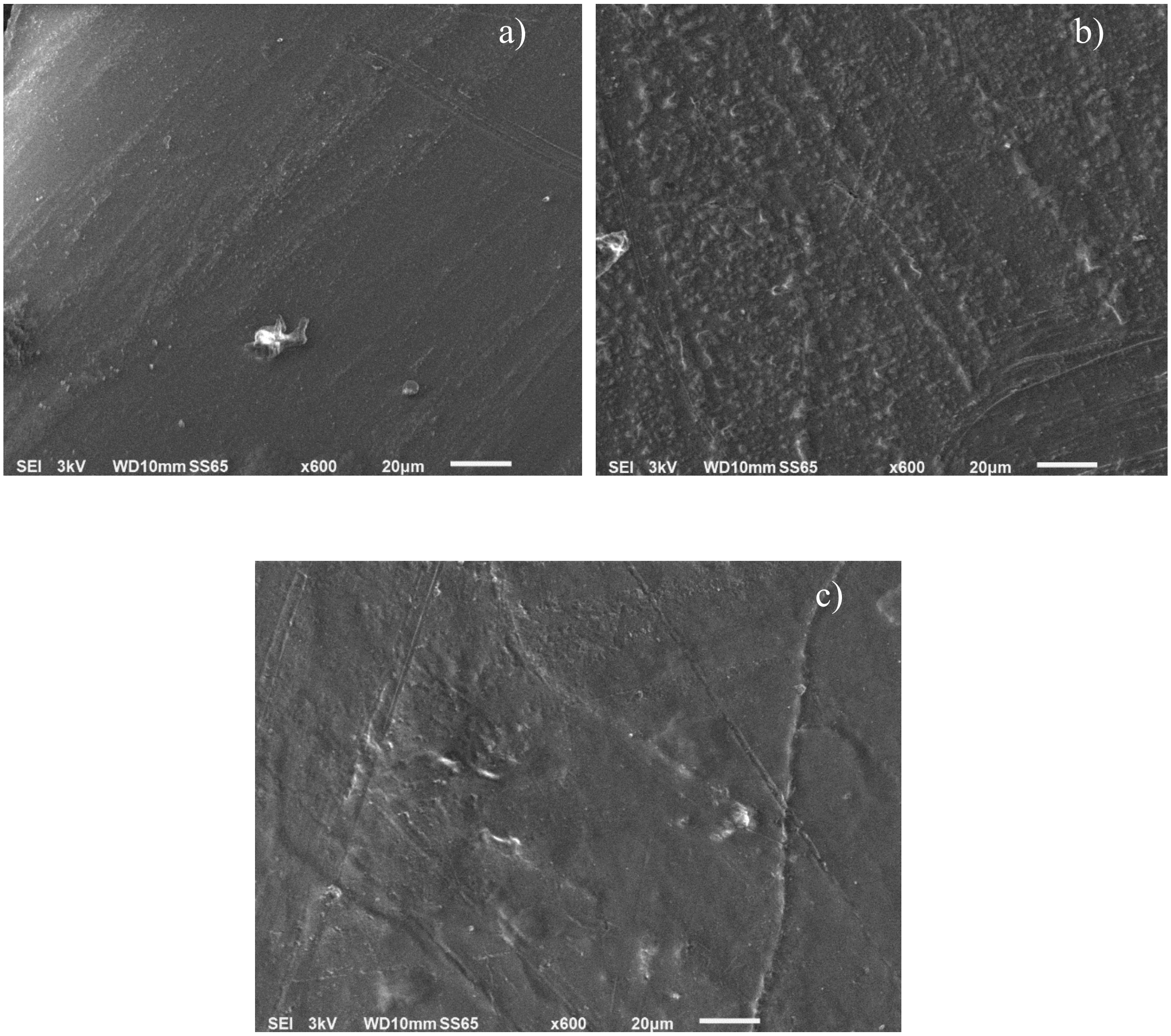

Figure 3. SEM micrographs of starch-based bioplastic: (a) control, (b) A_1 and (c) A_2.

Moreover, sample A_1 and A_2 have a smooth, compact, orderly surface, without the presence of pores which indicates that jicama starch and cellulose tend to form a homogeneous structure (Figure 3b and c). However, independent of the cellulose amount added, the surface is not entirely uniform since they are present particles that can it be explained by the insufficient time, agitation or temperature level used during the preparation of the filmogenic solutions.

Bioplastic Thermal analysis and Crystallinity Index

Thermal analyses is show in Table 2, DSC detected the melting temperature (T_m) due to state changes by application of heating rate. According to Luchese et al. (2015), T_m is related to a significant movement of the molecular chains due to the alteration of the crystals as the temperature increases.

Table 2: Thermal parameters and crystallinity index of starch-based bioplastic.

Sample	T_m (°C)	ΔHm (J/g)	% Xcc
Control	78.89	12.54	31.52
A_1	114.91	336.56	47.59
A_2	136.16	372.37	54.81

Adding cellulose to the polymer matrix increases the enthalpy and temperature of the samples composed with cellulose, indicating that bioplastic reinforced with this polymer improve their ability of resisting high temperatures, this in accordance with the report by Kaushik et al. (2010). The T_m and ΔH values were higher for A_2 (136.16 °C and 372.37 J/g) compared to the A_1 that presented a temperature of 114.91 °C and ΔH of 336.56 J/g, respectively. The results are similar to those found in mango fibrous endocarp starch and cellulose films, 128.65 °C and ΔH 236.43 J/g (Lorenzo- Santiago *et al*., 2016).

The control sample (starch/glycerol with no microcellulose addition) presented a crystallinity of 31.52%, and when cellulose was added, the crystallinity of the bioplastic increased for both A_1 and A_2 samples (Table 2). This behaviour may be due to a stabilizing effect in the interaction of cellulose fibre with amylose (Ma *et al*., 2005); the greater the crystallinity, the better thermal stability and fracture properties the material can acquire.

Conclusions

Microcellulose was extracted from coconut bagasse, from a chemical and mechanical method. The size of the microcellulose ranged between 40 and 400 μm. A control bioplastic and two starch-based bioplastic were made, reinforced with 0.05% cellulose (A_1) and 0.1% (A_2). Sample A_1 showed a melting temperature of 114.91°C, however, A_2 showed better thermal capacity, with a melting temperature of 136.16°C and an enthalpy of 372.37 J / g. The crystallinity of the A_1 and A_2 samples increased by 16.07% and 23.29%, respectively, compared to the control sample. Based on the results, it was shown that the bioplastic composed of 0.1% starch and cellulose (A_2), has good thermal characteristics. With this feature, the use of coconut bagasse microcellulose can be proposed as a 0.1% reinforcer in starch-based bioplastic to obtain materials with specific characteristics that can be used in the food industry, pharmaceutical, as coating, packaging, among others. The use and exploitation of coconut bagasse, will allow the waste generated are not considered as materials that have no commercial value.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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