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Production of Paper Using Bacterial Cellulose and Residue from the Sugar and Alcohol Industry

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The production of a fibrous surface formed from a composite of sugarcane bagasse and bacterial cellulose was the objective of this research. For this process the bagasse was grinded and cleaned, followed by the addition of a chemical substance capable of separating the cellulose fiber from the natural binders. The vegetable (VC) fiber originated from sugarcane bagasse (SCR) was mixed with bacterial cellulose (BC) fiber, which was produced in an alternative culture medium that used maize maceration liquor as a carbon and nitrogen source. The celluloses were ground, mixed and sieved to dryness. The resulting dry composite of the mixture was characterized by FTIR, DRX and TGA. The biomaterial obtained from the combination of BC and VC showed the same quality as a dense and rigid paper, with the advantage of not requiring the addition of chemicals and avoiding the consumption of a large volume of water. Infrared confirms the same chemical groups for BC and VC. Crystallinity and degradation did not show a large change for crystallinity index and degradation temperature when SCR was incorporated into BC. The pulp production process does not harm the environment at any time, since there is no emission of pollutants. An environmentally friendly product was obtained from sugarcane bagasse, a byproduct of ethanol and sugar manufacturing in BC mills and nanofibrils, producing high quality fibers, high purity and biodegradability, which makes the paper 100% recyclable.
Keywords: Bacterial Cellulose, *Gluconacetobacter hansenii*, Sugarcane Bagasse, Paper

1. Introduction

The pulp paper industries (PPI) are responsible for the release of wastewater containing very complex organic and inorganic pollutants, being ranked as the 6th most polluting industries in the world (Ugurlu et al., 2007). Its pollution is mainly caused due to the disposal of untreated or partially treated industrial waste to the aquatic ecosystem (Singh et al., 2019). Lignocellulosic waste consists of various complexes of organic and inorganic pollutants that are released as a byproduct of wood digestion and pulp bleaching process into the environment (Pokhrel and Viraraghavan, 2004).

Paper used to be produced by hand in mills by small-scale pulping. The leaves were formed on hand screens and dried outdoors or in the sun. The most important raw material in the paper industry is vegetable cellulose (VC). A natural polymer that is abundant in nature, found in the stem, fruits and leaves of plants.

Cellulose is formed by monomeric units of glucose. They contain characteristic compounds of an alcoholic group attached to a carbon atom neighboring a carbonyl group, which may be a ketone or aldehyde group. Thus, these glycids can be classified into monosaccharides, oligosaccharides and polysaccharides (Teixeira

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et al., 2017). The process of transforming sugarcane (*Sacharum officinarum*) into a finished product, such as alcohol or sugar, generates industrial waste such as bagasse, which can be processed and used in the production of paper. This innovative process allows the production of biodegradable paper of excellent quality and competitive market value with the papers that use pine and eucalyptus. According to CONAB (Brazilian Supply Company) approximately 3.7 tons of sugarcane bagasse are required to produce one ton of paper. Using other low-cost raw materials enables a more economically viable product. Cellulose is one of the most abundant polymers on the planet in its natural form, most of which is produced by plants however, various types of microorganisms are also capable of producing cellulose, like bacteria, by using specific culture media. Among many bacterial cellulose (BC)-producing bacteria, the most widely studied is the species *Glucanacetobacter xylinum*. A strict, non-pathogenic, gram-negative aerobic bacillus that can be found in fruits, vegetables and fermented products along with other microorganisms such as yeast, fungi and other bacteria (Rajwade et al., 2015).

BC produced from industrial waste has a cost of up to 78% lower than the cellulose produced with synthetic compounds. BC is a nanomaterial whose chemical composition resembles VC and presents itself as a fibrous raw material and a well-structured morphological arrangement, high crystallinity and heat resistance. It is a peculiar form of cellulose as it has nanometric properties and a crystalline structure (Oskman et al., 2016). Bacterial cellulose has high purity since when it is obtained, as it is not associated with other components, such as lignin and hemicellulose from the VC (Costa et al., 2017, Sanchez et al., 2010).

BC's production using alternative medium like with agro-industrial waste such as corn steep liquor (CSL) or fruit residues, reduces the cost of producing BC nano fibrils and maintains properties for application in various industrial segments (Amorim et al., 2019; Costa et al., 2017, Kiziltas et al., 2015).

Bacteria can use sugarcane bagasse (SCR) as a raw material for the production of BC, resulting in the making paper-like fibrous surfaces. Given that Brazil is a major producer of sugarcane and its production has increased greatly in recent years to meet global demands for sugar and bioenergy production. The 2018/2019 sugarcane harvest production in Brazil was estimated at around 625.96 million tons of sugarcane (CONAB, 2018; Galdino et al., 2019; Bordonal et al., 2018).

BC was initially reported by Brown in 1988. It was identified the growth of unbranched film with the chemical cellulose equivalent structure of plants (Esa et al., 2014). It was also associated that VC differs from its biological pair mainly due to its micrometric fiber character, while BC has nanometric fiber character and is extracted through the bacterial cell wall (Donini et al., 2010). Visually, the difference between them both refers to its appearance and water content. VC has a fibrous appearance, while BC resembles a hydrogel. However, the functional groups that characterize BC are the same as those of VC.

With that being said, the production of a fibrous surface formed from a composite of sugarcane bagasse and bacterial cellulose was the objective of this research.

2. Materials and Methods

Microorganism and culture conditions - for BC production, a strain of *Gluconacetobacter hansenii* UCP1619, obtained from the culture collection of Nucleus of Resource in Environmental Sciences, Catholic University of Pernambuco, Brazil, was used. The standard culture medium used in the experiments was the HS described by Hestrin and Schramm (1954) and modified by Hungund and Gupta (2010). The liquid medium contained 2.0 % glucose (w/v), 0.5 % yeast extract (w/v), 0.5% peptone, 0.27 % Na_2HPO_4 (w/v), and 0.15 % citric acid (v/v). For the production of BC, the bacterium was cultivated in an alternative medium (Costa et al., 2017), in which the carbon source was reduced by 25% and synthetic nitrogen was completely replaced with (CSL): 1.5 % glucose (w/v), 2.5 % CSL (w/v), 0.27 % Na_2HPO_4 (w/v), and 0.15 % citric acid (v/v).

2.1 Synthesis of Bacterial Cellulose

3 % of the inoculum produced with *Gluconacetobacter hansenii* was inoculated in a semi-capped glass vessel (250 mL) containing 100 mL of the different liquid media, and then statically incubated at 30 °C (BC produced in HS medium) and at 30 ^{o}C (BC produced in alternative medium formulated CSL) for 10 days (Gomes et al., 2013; Wu et al., 2014). After cultivation, the BC pellicles were sent for cleaning and purification (NaOH 1.0 M). Determination of thickness, hydrated mass, and dry mass was done. Then, the pellicles were washed with deionized water several times to warrant the complete remove the alkali, leaving the pellicle at neutral pH (Figure 1A).

2.2 SCR Purification

Wet SCR was ground in a knife mill and punched in a 60 °C oven for 12 hours. 1.5 L of 3 % NaOH was added at 80 °C for one hour. After complete lignin removal, the material was neutralized to pH 7 (Figure 1B).

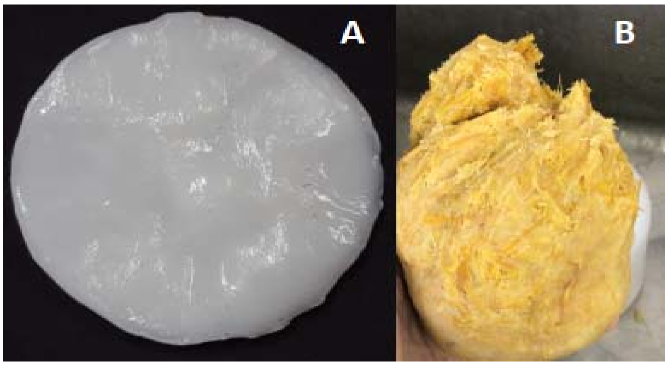

Figure 1 Membrane of purified BC (A) and sugarcane bagasse (SCR) (B)

2.3 Paper production

For paper production, compositions of 25, 50 and 75% BC and 75, 50 and 25% VC were used. The BC membranes were ground in a high speed Spolu industrial blender under stirring at 18,000 rpm for 2 minutes. Then the treated bagasse was added. The stirring process continued for a further 2 minutes until the material appeared as a homogeneous mixture. Excess water was removed with a 230 mesh sieve and distributed in 3 cm thickness in Petri dishes, as demonstrated in Figure 2.

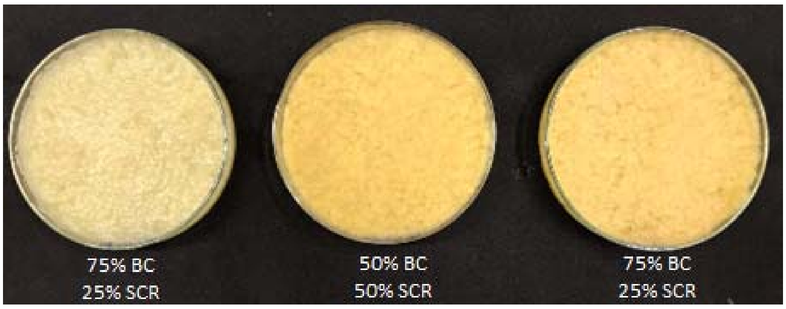

Figure 2 Paper samples prepared with varied BC and SCR composition

2.4 Paper drying

The material was oven dried at 60 °C for 48 hours.

2.5 X-ray diffractometry (XRD)

The XRD patterns of the blends were measured using a Phillips X'pert MPD diffractometer with CuαK radiation. The percentage of crystallinity was measured as x (%) = (Imax - Imin) / Imax x 100 %, in which Imax is the height of the peak at 2θ = 22.5 ° and Imin is the valley between the peaks at 2θ = 22.5 ° and θ = 16.3 ° (Gomes et al., 2013).

2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo analyzer on samples weighing approximately 8 mg. Each sample was scanned along a temperature range from room temperature to 600 °C with a heating rate of 10 °C/ min and a flow rate of 20 mL/ min to avoid the oxidation of the sample (Kiziltas et al., 2015).

2.7 Attenuated total reflectance and Fourier-transform infrared (ATR/FTIR) spectroscopy

Prior to the analysis, the blends were placed in a desiccator containing silica gel for two weeks at room temperature to maintain the films dehydrated. The films were digitized with a Bruker FTIR spectrometer (Equinox 55 Model, Bruker Co., Ettlingen, Germany). The samples were measured in a horizontal ATR device through a crystalline cell plate (45 ° ZnSe, 80 mm in length, 10 mm in width and 4 mm in thickness) (PIKE Technology Inc., Madison, WI, USA). Analyses were conducted to identify functional groups in the samples and analyze the interactions among the BC/SCR in a spectrophotometer between 4000-400 cm^{-1}. All spectra were recorded after 32 scans with a resolution of 4 cm^{-1} (Limpan et al., 2012).

3. Results and discussion

After the drying process, it was observed that the final produced papers presented a yellow coloration that approximates the color of the SCR. That is directly related to sugarcane species and variety, growth location, edaphoclimatic conditions and cultural treatments, by macroscopic analysis.
The paper produced with 75 % BC membranes and 25 % VC obtained from sugarcane presented itself as a flexible material. As the percentage of sugarcane bagasse increased to 50 and 75% the paper became thicker, stiffer and more brittle, making folding difficult.
Differential thickness results reflects the paper composition. Paper produced with 75% BC presented a thickness of 1 cm while 50 and 75% were of 1.5 and 2 cm respectively.

3.1. Fourier-transform infrared (FTIR) spectroscopy

Figure 3 shows the infrared spectra for pure SCR bagasse and additive BC films. It is noticed that in the spectra graphs did not show the appearance of new characteristic peaks. This behavior can be explained by the similarity in the structures of BC and SCR which also consists of plant cellulose.

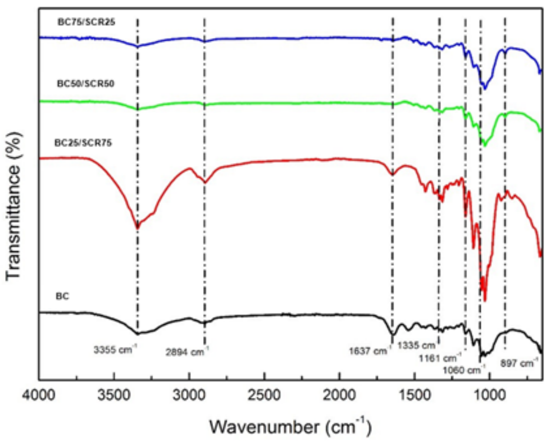

Figure 3 Spectra of BC75/SCR25, BC50/SCR50, BC25/SCR75 and BC

3.2. X-ray Diffraction (XRD) Analyses

The crystallinity index (CI) was calculated based on the peak intensity, as shown in Figure 4. The CI obtained for the BC100/SCR0 mhesed BC was 55 % while for BC75/SCR25 was 32 %, BC50/SCR50 29 % and BC25/SCR75 33 %. Confirming that the increase in the percentage of SCR for the production of the fibrous surface, the variation in CI is very low.

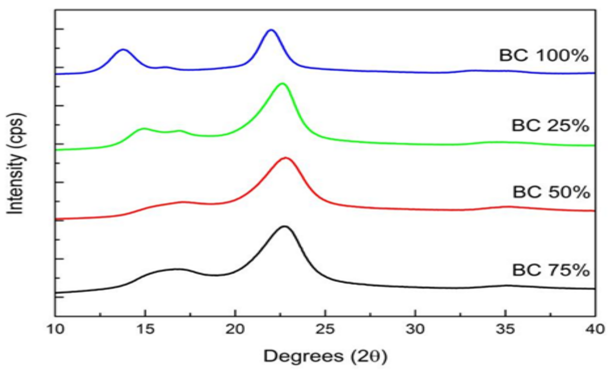

Figure 4 XDR graphics of BC75/SCR25, BC50/SCR50, BC25/SCR75 and BC100/SCR0

3.3. Thermogravimetric analysis (TGA)

Table 1 presents the thermal degradation parameters of SCR-additive BC. It was observed in the thermograms of polymeric films three stages of degradation (Figure 5). The first stage demonstrates dehydration by removing the remaining water from the polymer matrix of the drying process. The second stage is attributed to SCR thermal degradation and the third stage refers to BC degradation, as described in the literature (Sanchez et al. 2010; Yin et al., 2019).

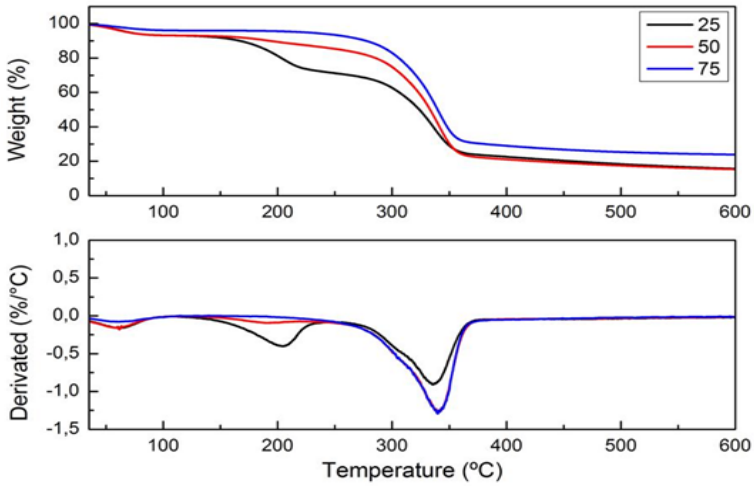

Figure 5 Thermogravimetric analysis graphics of BC75/SCR25, BC50/SCR50, BC25/SCR75 and BC100/SCR0

Table 1. Thermal decomposition of samples of BC25/SCR75, BC50/SCR50, BC75/SCR25 and BC100/SCR0 (data obtained from TGA curves).

Samples	Stage 1 (°C)			Stage 2 (°C)			Stage 3 (°C)		
	T_{onset}	T_{endset}	T_{max}	T_{onset}	T_{endset}	T_{max}	T_{onset}	T_{endset}	T_{max}
BC25/SCR75	25	78	64	173	219	204	295	356	336
BC50/SCR50	24	78	63	162	218	188	228	360	341
BC75/SCR25	24	78	59	-	-	-	274	358	342
BC100/SCR0	35	99	53	-	-	-	294	340	323

As the SCR concentration increases, the initial degradation temperature on the 3rd stage approaches the pure BC temperature. Concentrations of 25 and 50% of SCR have greater influence on the thermal properties of BC. When the maximum and final degradation temperature is observed, the obtained values are higher when compared to the pure BC matrix. Thus, the maximum SCR concentration maintained its thermal properties.

4. Conclusion

The fibrous material produced from the composition of BC and SCR is presented as a material with paper-like visual characteristics. The potential use of BC in industrial production of paper is considered by the study. Future research should evaluate BC and VC percentages, sugarcane variety, both fiber processing, amount of water, drying and sequential handling that may differ in the outcome of sustainable paper production. One of the tools for the transformation of the former is the action that integrates agro-industrial waste and BC which is a degradable and low production cost biopolymer.

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