CHARACTERIZATION OF LIGNOCELLULOSIC MATERIALS EXTRACTED FROM THE BANANA PSEUDOSTEM

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Resumo

Nowadays, agro-industrial wastes utilisation is in consonance with the development of new products, including nanotechnological added-value ones. In this context, fibres from banana pseudostem appear as an interesting source for cellulose nanowhiskers (CNW). The aim of this work was to evaluate the effects of chemical treatments over structural modifications on the fibre after by thermogravimetric (TG) analysis. It was determined through fibre chemical characterisation that there is a relative high percentage of extractives into the crude fibre, that might be removed due to chemical cleaning. After the chemical treatments, it was noted an elevation in the fibre thermal stability, broadening the possibilities of its applications, specially incorporating it into plastic matrices.

Introduction

There are several concerns about many of the current materials that are oil-derived. In this context, there is a great survey for natural products that can substitute them. A good example of this situation is the utilisation of natural fibres into composites for replacement of glass fibres or plastics. Plant fibres are renewable, biodegradable and do not show health hazards. However, they are difficult to mix with some matrices, as a result of both fibres and matrices characteristics. Therefore, this poor interaction can affect, for instance, some material properties, as the thermal stability.

Many kind of plants were evaluated as sources of new materials or as reinforcement in some traditional materials, for instance coconut husk (ROSA et al., 2010), sisal fibres (MORAN et al., 2008), sugarcane bagasse (CAO et al., 2006), cotton linter and softwood pulp (CLARAMUNT et al., 2010).

In Brazil, there is a great generation of byproducts on the countryside, especially after the harvest of the main economical commodity. In the banana fields, there is a huge generation of wastes as a consequence of the plant life-cycle, because pseudostems, hangers and leaves are not economically used. They can be used as livestock feed, for handicraft works or even as a natural manure on the soil. However, when they cannot be used for none of these alternatives, they are thrown away without caution, disturbing the environment, and may become a focus of disease vectors. It is estimated that Brazilian banana production is about 7,116,808 tonnes/year, what gets a potential biomass of same scale which is left in the countryside (FAO, 2010)

Nanotechnology is the study of matter with at least one dimension at the scale of 100 nm or less. (KAMEL, 2007, WEGNER et al., 2006). Although natural fibres are good fillers for polymeric matrices, cellulose nanowhiskers provides better mechanical properties. As a comparison, man-made cellulose fibres have a Young´s modulus of about 30 GPa, whilst cellulose nanocrystals present, experimentally, a Young´s modulus of about 114 – 134 GPa. Thus, the agro-industrial wastes are aligned with this recent and growing industrial demand for renewable materials, and banana pseudostem is an attractive source of such ones (GANSTER; FINK, 2006; WU et al., 2007; ZIMMERMAN et al., 2010).

There are several referenced chemical treatments for nanocellulose extraction, but the most used one is the alkaline treatment, sometimes named mercerisation, in which the fibre is immersed into a concentrated NaOH solution (QIN et al., 2008; ROSA et al., 2010). Another treatment, that is also used in paper and cellulose industries, is the bleaching by hydrogen peroxide, degrading lignin and hemicellulose matrix, releasing the cellulose fibres. Afterwards, the cellulose is subjected to an acidic treatment, to reduce the polymeric chain to the desirable size (KAMEL et al., 2007; ORTS et al., 2005). The amorphous domains are promptly hydrolysed, resulting only in the crystalline domains. Moreover, when it is used sulfuric acid, it provides a superficial negative charge on the crystals, creating an electrostatic repulsion among them, increasing the suspension stability.

The aim of this work was to evaluate the modification at the thermal stability of the raw fibre, the bleached one and the cellulose nanowhiskers from banana pseudostem fibres and to correlate this modifications with the cellulose content of the materials.

Experimental

Chemical treatments

Banana pseudostem passed by several treatments. Initially, the pseudostem were pressed, resulting fibres from 5 cm to 40 cm. They were dried at an air circulating oven at 55ºC for 7 days. Afterwards, they were chopped in a Wiley mill and sieved through a 35-mesh sieve.

A portion of this ground powder was mercerised in a 5% NaOH solution (w/v), in a ratio of 5 g of powder for 100 mL of solution, stirred for 2 hours at room temperature. The sample was washed with tap water until it reached pH 7.0 and then it was washed twice with distilled water. The sample was dried at an air circulating oven at 45ºC for 24 hours. For bleaching, 5 g of the mercerised powder was stirred at 50-55ºC for 2 hours in 100 mL of a H_2O_2 7,2% (w/v) and 4% NaOH (w/w) solution. The washing step was performed as the same as the mercerisation washing.

Cellulose nanowhisker extratcion was performed as described by Orts et al. (2005) with modifications. The mass of 5 g of bleached fibre was vigorously stirred in 100 mL of a 60% sulphuric acid (w/w) solution at 45ºC for 130 minutes. At the end of this time, the reaction was halted by casting a 5 times volume of deionised cold water. The suspension was sonicated for 2 minutes and centrifuged at 12,000 rpm for 10 minutes, discarding the supernatant and washing the precipitant with deionised water. This process was repeated more twice. The nanocellulose suspension was dialysed against a continuous flow of tap water, until raising of the pH from 1.8 until 6.0-7.0.

Chemical characterisation

It was determined the percentage of moisture, ashes, extractives and holocellulose from the raw and the bleached fibre, in accordance with the following methods (Table 1).

Table 1: Analysed components and applied methodology.

Component	Methodology
Moisture	TAPPI T 550 om 03(2008)
Ashes	TAPPI T 413 om 93 (1993)
Extractives	TAPPI T 204 cm 97 (1997)
Holocellulose	YOKOYAMA et al., 2002

Thermogravimetric (TG) Analysis

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out in a TGA/SDTA 851 METTLER TOLEDO equipment. It was used about 4.0 mg of plant material and an alumina sample holder. The experimental conditions were: temperature range from 25ºC to 800ºC, heating rate of 10ºC min^{-1} and synthetic air atmosphere flow of 50mL/min.

Results and Discussion

Chemical characterisation

The chemical characterisation presents a high content of extractives and ashes in the raw fibre. After the bleaching, they were greatly reduced, therefore increasing the holocellulose content, and as well as the nanocelulose yield and quality (Table 2).

Table 2: Chemical characterisation of raw and bleached fibres of banana pseudostem

Component	Raw Fibre	Bleached Fibre
	Percentage content (mean ± standart error)	
Moisture	8.46 ± 1.12	7.26 ± 0.18
Ashes	13.54 ± 0.32	2.11 ± 0.17
Extractives	23.14 ± 8.30	2.41 ± 0.01
Holocellulose	43.25 ± 3.59	79.44 ± 0.36

Thermogravimetric (TG) Analysis

The graphics from TG and DTG analyses present three main events. The first one is related to loss of the sample moisture. Due to the cellulose hydrophicity, there is a higher water retention in the bleached fibre and in nanocellulose, as one can note by the broader amplitude in these samples, in comparison with the raw fibre.

The second main event is related to cellulose and hemicellulose pyrolyses. One can note that the hemicellulose removal from the raw fibre contributes to increase the pyrolysis resistance as for the bleached fibre as for the nanocelulose. Moran et al. (2008) report that, in inert atmosphere, hemicellulose and lignin are the first components to degrade, by 200ºC. Hemicellulose persists until 315ºC, whilst lignin persists until 700ºC. Even in oxidative atmosphere, the results present similarities. For nanocellulose, there is also an influence of the esterification of hydroxyl groups during the acidic hydrolysis, which lows the activation energy for cellulose degradation, what reduces the pyrolysis resistance of the sample (TEIXEIRA et al. 2010).

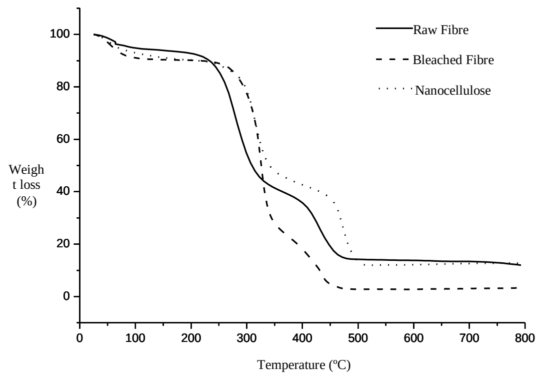
The last event is major related to lignin pyrolysis, and minor related to the inner cellulose bounds (ROSA et al. 2010). The cellulose degradation begins at 315ºC and goes on until 400ºC, in a inert atmosphere (MORAN et al., 2008). The third peak in DTG for the raw fibre is due to the lignin content, which acts as a pyrolysis retardant, broadening the endset until after the endset of the same peak for the bleached fibres. The presence of residual lignin in the nanocellulose sample, in association with the higher cellulose content of the three materials, might be the reason for its higher stability. Since the bleached fibres have a lower lignin content than the raw fibres and a lower cellulose content than the nanocellulose, this material presents the lower endset, but it is an intermediary T_{max}, between the other two samples.

Table 3 presents the data of the onset degradation temperature (T_{onset}), the endset degradation temperature (T_{endset}) and the maximal weight loss point (T_{max}), which represent the peaks in the DTG graphic (Figure 1).

Table 3: Characteristic temperatures of thermogravimetric events of banana pseudostem raw fibre, bleached fibre and extracted nanocelulose

Sample	1st Event		
	T_{onset} (ºC)	T_{endset} (ºC)	T_{max} (ºC)
Raw Fibre	39.08	83.67	---
Bleached Fibre	35.34	81.68	---
Nanocelulose	35.84	87.96	---
	2nd Event		
	T_{onset} (ºC)	T_{endset} (ºC)	T_{max} (ºC)
Raw Fibre	247.80	308.94	280.17
Bleached Fibre	304.51	338.71	326.00
Nanocelulose	289.21	335.52	316.17
	3rd Event		
	T_{onset} (ºC)	T_{endset} (ºC)	T_{max} (ºC)
Raw Fibre	408.56	459.59	428.00
Bleached Fibre	420.34	448.15	436.50
Nanocelulose	461.55	491.31	472.50

(a)



(b)

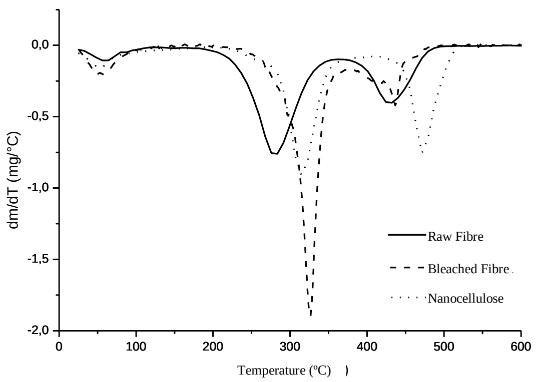


Figure 1: Graphics of TG (a) and DTG (b) of banana pseudostem raw fibre, bleached fibre and extracted nanocellulose.

Conclusion

The chemical treatment (mercerisation and bleaching) is efficient to reduce the contents of non-cellulosic components, as extractives and ashes, raising the holocellulose percentage, what potentially raises the yield of nanocellulose extraction.

The thermal stability raises as a function of the elevation of cellulose content, what becomes the banana pseudostem fibres and nanocellulose suitable for industrial application, for instance, incorporating in plastic matrices.

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