SYNTHESIS AND CHARACTERIZATION OF HYBRID FIBROUS AND THEIR POTENTIAL USE AS FILLER IN COMPOSITES

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Abstract: In Brazil, banana cultivation (*Musa sapientum*) generates large amounts of waste consisting of cellulose, hemicellulose and lignin. Lignocellulosic fibres have important features such as biodegradability, low toxicity, non-abrasive, low density and good specific mechanical properties, justifying their potential as substitute for synthetic fibres in applications, such as reinforcement in polymeric composite. However, the presence of hydroxyl group and low thermal stability of natural fibres may limit their use for this application. Some authors report the use of chemical and physical treatments in the fibres to improve the adhesion to the matrix. From the chemical treatment of banana fibres with a mixture of acetic and nitric acids it was possible to isolate the semicrystalline cellulose. This study aims to use isolated pulp of banana fibres like organic matrix of a fibrous hybrid material containing hydrous magnesium oxide in mass proportions equal to 2% and 3%. The generated hybrids were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR). TGA curves show that thermal degradation of main fraction of material occurred at higher temperatures. XRD curves indicate that the hybrids have different characteristics from their precursor. FTIR analyzes show that the chemical treatment with acetic acid induced partial acetylation of banana fibre.

Keywords: Hybrid, filler, fibres, composites.

1. INTRODUCTION

Composite materials have huge applicability in several technological fields, including construction industry which is their main consumer in Brazil, followed by the sectors of wind power generation, aerospace among others [1-2]. Traditional building materials are increasingly being replaced by advanced composites, e.g. fibre reinforced polymers (FRP) and fibre reinforced cement (FRC) [3]. The class of polymer composites has also been widely used in the automotive and packaging industry due to the requirement of low density materials with good specific mechanical properties and chemical resistance [4-6]. In the past few years, issues concerning environmental preservation, such as waste disposal and the depletion of non-renewable resources led the focus of researchers to the alternatives feedstocks that can substitute or act like fillers in synthetic polymers in order to decrease the amount of petroleum-derived plastics [7].

Countries such as China, India, United States, Brazil and Nigeria are among the world's largest producer of agriculture products, which include cereal, vegetable and fruits [2]. Agricultural farming-wastes are an important source of biomass, reuse them is as necessary as economically viable due to the wide availability of these resources and the high cost generated by its disposal [4]. The tree major

chemical components of biomass, cellulose, hemicellulose and lignin are utilized in many applications, such as biofuels and biomaterials, including conventional composites and novel nanocomposites [8]. Lignocellulosic fibre, such as flax, hemp, kenaf, henequen, banana, oil-palm, and jute have drawn considerable attention as substitutes to synthetic fibres, such as glass and carbon fibres [9]. The banana plant fibres are fibrous residue of pseudo-stems and leaves lefts over after the banana cultivation. Banana cultivation generates a considerable amount of cellulosic-based waste. The comestible part, the fruit, constitutes only 12% by weight of the plant. The remaining parts become agricultural waste, which is lignocellulosic in nature. This residual resource has attracted much interest due to the potential use as a reinforcing component in high performance composite materials [10].

Natural fibre composites are proposed to substitute synthetic fibre composites due to several advantages such as biodegradability, abundant, corrosion resistance, non-toxicity, competitive mechanical properties, less abrasiveness to processing equipment, reduced energy consumption and minimum waste disposal problems [9]. However, there are some limitations associated with the use of natural fibres as reinforcement in polymer composites. These includes the high moisture absorption and incompatibility between fibres and polymer matrices, inferior fire resistance, limited processing temperatures and difficulty in using established manufacturing process [3-4]. The adhesion between the fibre-matrix plays a significant role in the final mechanicals properties of the composites since the stress transfer between matrix and fibre determines the reinforcement efficiency. The major cause for this drawback is the presence of hydroxyl and other polar groups in natural fibres which makes them hydrophilic in nature [3-4]. To improve adhesion, the natural fibres are usually surface treated [6].

A number of surface modification methodologies have been attempted. Some of them not only improve interaction between fibre and polymer matrices, but also reduce moisture absorption. Surface modification typically involves one of four (chemical, physic-chemical, physical and mechanical) methods. Several research groups have studied chemical treatments in natural fibres, e.g. alkaline treatment, silane treatment, acetylation, peroxide treatment, sodium chlorite treatment, among others [11]. Other drawbacks that must be overcome are low thermal stability and poor fire resistance of natural fibres. Some authors suggest as an alternative the hybridization of natural fibres with additives (mineral fillers). It was found that the application of antioxidants and fire retardants had a positive effect on the performance of composites [12]. Certain inorganic materials decompose endothermically with the release of inert gases or steam, enhancing the potential fire retardant effect. In practice, most of the suitable materials are group II or III carbonates or hydroxides, such as $Mg(OH)_2$ and $Al(OH)_3$. They have three fire retardant effects: endothermic decomposition, production of inert diluent gases and accumulation of an inert layer on the surface of the decomposition polymer [13].

The present work is dedicated to prepare and characterize hybrids fibrous materials produced by the introduction of inorganic additives in an organic matrix. The organic matrix consists of cellulose extracted from banana fibres and the hydrous magnesium oxide, as additive, added in mass ratios 2 and 3 (w/w %). In addition, the influence of banana fibres surface modification on its structure and the potential of using hybrid fibrous as fillers in composites will be evaluated.

2. MATERIALS AND METHODS

2.1. Materials

Banana leaves were provided by EEL-USP (Laboratório de Novos Materiais) and the following chemicals used in this study were of analytical grade: acetic acid (glacial), sodium hydroxide, nitric acid (65% w/v), magnesium chloride hexahydrate and silver nitrate. Solutions of acetic acid (80% v/v), sodium hydroxide (1 M) and silver nitrate (0,05 M) were prepared from the chemicals using deionized water.

2.1. Isolation of cellulose

Natural fibres used in this work are the species *Musa sapientum.* Banana leaves were washed, dried at room temperature and mashed. The chosen chemical treatment is a [14] adaptation by [15]. Lignocellulosic fibres were extracted from banana leaves using a mixture of solutions of acetic acid and nitric acid. The reaction was performed at 120 ^{o}C for 20 minutes under stirring. The procedure was repeated to remove most of the amorphous fraction of vegetable fibres. The pulp was then filtered and washed with deionized water until pH~7, subsequently washed with ethyl alcohol and dried in an oven at 60 ^{o}C until a constant weight was achieved. The material was then ground to a particle size equal to 20 mesh.

2.2. Synthesis of MgO.nH$_2$O

MgO.nH$_2$O was obtained from MgCl$_2$.6H$_2$O by co-precipitation method using NaOH 1M solution as precipitant agent. The precipitant was added to the aqueous medium until pH 11 [16]. After the precipitation, the product was washed with deionized water and dried in an oven at 50 ^{o}C.

2.3. Synthesis of hybrid fibrous (Cel/MgO.nH$_2$O)

Cel/MgO.nH$_2$O hybrids were prepared from 2g of cellulose, in two different proportions with amounts of MgO.nH$_2$O corresponding to 2% and 3% to the total mass of the hybrid. About 0,22g of MgCl$_2$.6H$_2$O was dissolved in 50 mL of deionized water to obtain the hybrid 97 Cel/3 MgO.nH$_2$O and 0,14 g of MgCl$_2$.6H$_2$O to give the hybrid 98 Cel/2 MgO.nH$_2$O. The hybrid was synthesized according to MgO.nH$_2$O synthesis, however with the addition of cellulose previously swollen in water for 1 hour. The procedure was repeated for both proportions of additive.

2.4. X-ray diffraction

The X-ray diffraction (XRD) scans were recorded at room temperature using CuKα radiation (λ=1,5405980) within a range for 2θ of 10 – 90°.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out at 20 ^{o}C/min under synthetic air flow within a range of 25 – 900 ^{o}C using a thermobalance Shimadzu, TGA-50 in order to evaluate the thermal decomposition profile of the materials analyzed, as well as identify the bands corresponding to events with the highest weight loss of the samples. About 5 mg of sample was used in each test.

2.6. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the samples were recorded to assess the influence of chemical treatment employed in the structure of the banana fibres. The analysis was carried out using diffuse reflectance infrared Fourier transform (DRIFT).

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis

The XRD patterns of cellulose, $MgO.nH_2O$ and hybrid 97 Cel/ $3MgO.nH_2O$ are shown in Fig. 1. Pulp pattern showed a broad peak at $2\theta=22°$, which can be ascribed to the high intensity (002) plane of cellulose. Smaller peaks at $2\theta=15°$ and $2\theta=35°$ were also observed, corresponding to the (101) and (040) planes. The organized structure of the inorganic oxide is reflected in its pattern with narrow and sharp peaks. The hybrid 97:3 pattern is similar to cellulose except for the intensities of characteristics peaks. This profile was expected due to the hybrid weight ratio, predominantly composed of cellulose.
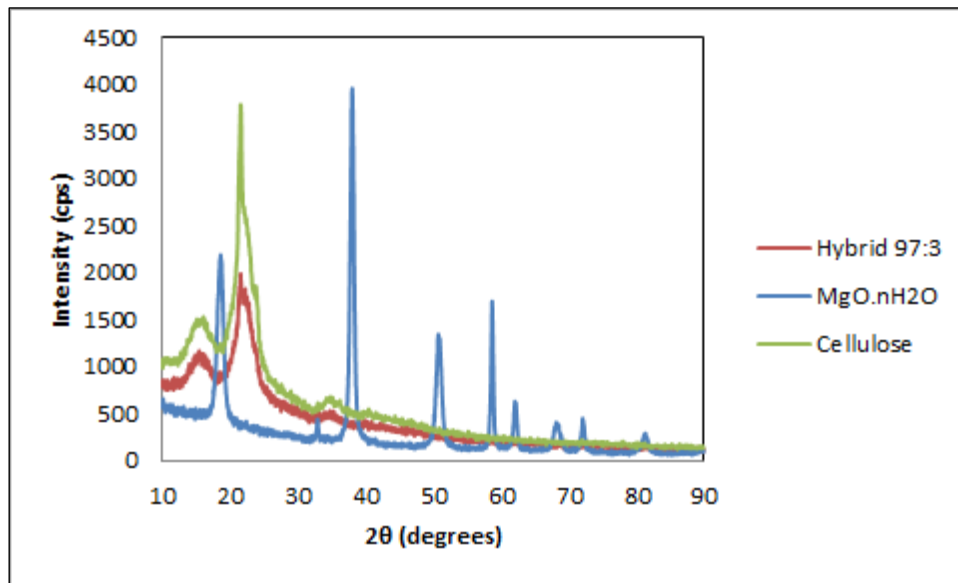

Fig. 1 – XRD patterns for cellulose, $MgO.nH_2O$ and hybrid 97 Cel/3 $MgO.nH_2O$.

Fig. 2 shows the XRD patterns of cellulose, $MgO.nH_2O$ and hybrid 98 Cel/ 2 $MgO.nH_2O$. The increase in the cellulosic fraction has the hybrid 98:2 pattern more similar to that of the cellulose. No characteristic peak of crystalline magnesium oxide was observed in the XRD patterns of any weight ratios tested for hybrids, indicating that the incorporation of inorganic additive in the organic matrix was successful.
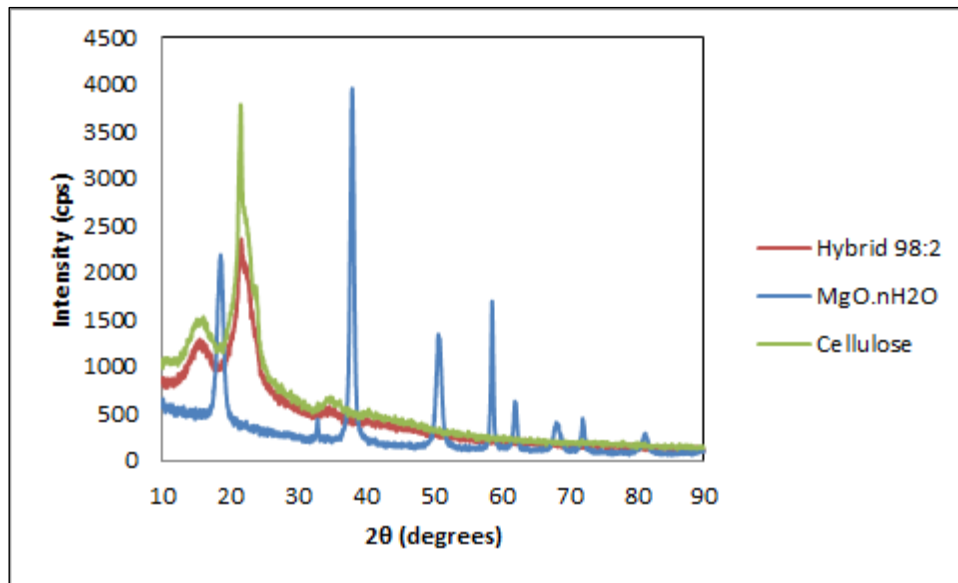
Fig. 2 – XRD patterns for cellulose, $MgO.nH_2O$ and hybrid 98 Cel/2 $MgO.nH_2O$.

3.2. Thermogravimetric analysis

TGA/DTG analysis was used to evaluate the thermal stability of cellulose and the organic-inorganic hybrids. The recorded TGA curves of the different materials are plotted in Fig. 3 (a) and (b), while additional data are summarized in Table 1.
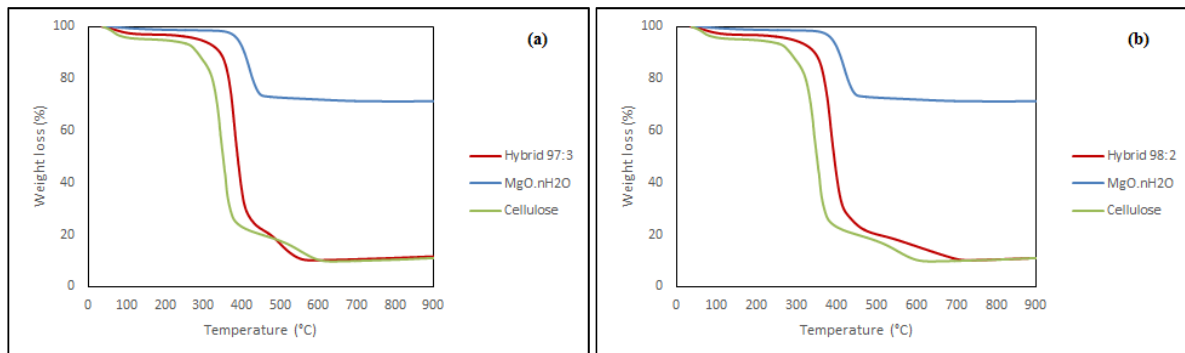

Figure 3 – a) TGA curves of cellulose, $MgO.nH_2O$ and hybrid 97 Cel/3$MgO.nH_2O$; b) TGA curves of cellulose, $MgO.nH_2O$ and hybrid 98 Cel/2 $MgO.nH_2O$.

Three stages of weight loss are associated with the cellulose and hybrids TGA curves (Fig. 3a and 3b). A first stage to cellulose, up to ~160°C, corresponds to the adsorbed water content, released at about 62 °C according to the DTG peak (Table 1). The weight loss in this step is minimal due to the surface modification which reduced hydrophilic nature of organic matrix [15]. Second stage occurs at temperatures between 160 and 465°C and is related to the crystalline cellulose decomposition. The major fraction of pulp is lost in this step (~75%) which indicates that the crystalline cellulose was successfully isolated from raw banana fibres. Temperature of DTG peak show that the maximum weight loss occurs at 348°C to cellulose (Table 1). Third decomposition stage of pulp occurs at temperatures less than 900°C, it can be attributed to depolymerization of polymeric chains of cellulose.

Thermal decomposition of $MgO.nH_2O$ covers 2 stages of weight loss. First stage, up to 248 °C is related to the elimination of the adsorbed water on the oxide surface that occurs at 70 °C. The second stage refers to the loss of structural water of the hydrous magnesium oxide; the maximum weight loss rate is given to DTG peak at 420°C (Table 1). For the amount of material lost in this step, it was estimated that is one molecule of hydration water in the generated oxide.

The hybrids show thermal behavior similar to the cellulose, as they are mainly made of pulp. However, the amounts of $MgO.H_2O$ added to the matrix have shifted DTG peaks to higher temperatures for the hybrids compared with cellulose, as can be seen in Table 1. The second step of weight loss has the most significant change due to the influence of addition of $MgO.H_2O$. It can be related to the temperature at which the hydrous oxide lost their structural water. With the incorporation of inorganic additive, a larger fraction of the material is lost at temperatures much higher than the isolated cellulose (~385°C) in both proportions. Also, the third stage of decomposition affects a bigger fraction of hybrids (> 21 wt%) than the cellulose (~8 wt%) due to the presence of the inorganic material.

Table 1: TGA data of the different materials.

Material	Temp. range (°C)	Weight loss (%)	DTG temp. (°C)	Residue (%)
$MgO.H_2O$	25 - 248	1,35	70	71,3
	248 – 900	27,7	420	
Cellulose	25 - 160	4,92	62	
	160 – 465	75,7	348	11,0
	465 - 900	8,40	551	
Hybrid 97:3	25 – 171	3,09	65	
	171 – 461	75,7	382	11,6
	461 – 900	21,3	499	
Hybrid 98:2	25 – 171	3,20	66	
	171 – 442	71,6	388	11,0
	442 - 900	25,2	591	

3.2. Fourier transform infrared spectroscopy

FTIR spectroscopy analyses of untreated banana fibre and the cellulose samples reveal that compositional changes occur in the fibre structure during the treatment with CH_3COOH/HNO_3. The prominent band at 3600 cm⁻¹ that is seen in both spectra corresponds to the –O-H group. Banana fibres spectrum have the larger band in this region of wavelength while cellulose spectrum have a narrower band. This implies that the moisture content on the samples may differ due to removal of amorphous components of banana fibres and decrease of the hydrophilic group amount [10]. A peak at 1740 cm⁻¹ in cellulose spectrum can be attributed to –C=O stretching, which is characteristic of esters. No

equivalent peak was displayed in the banana fibres spectrum, indicating that the chemical treatment results in partial acetylation of cellulose [15].
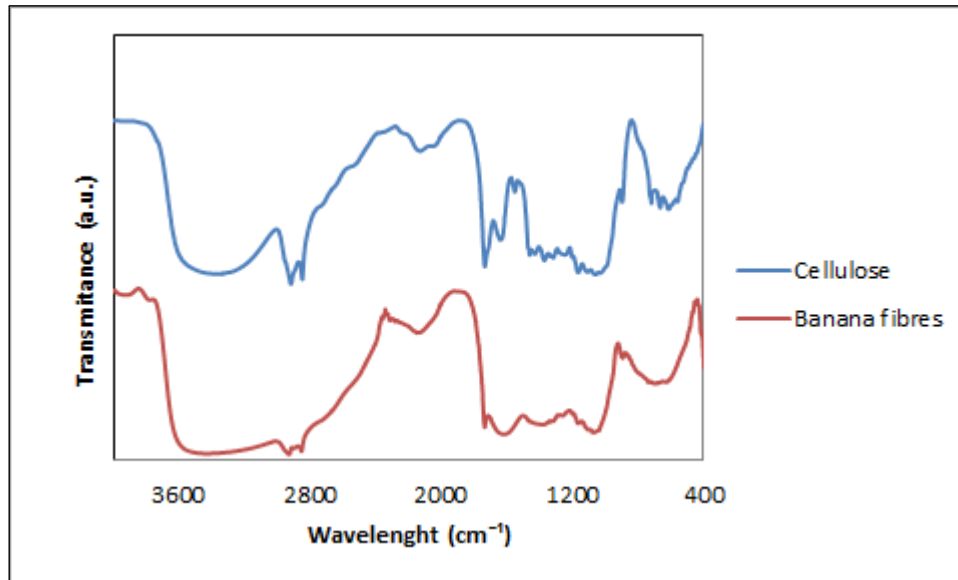

Figure 4 – FTIR spectra of banana fibres and the cellulose after chemical treatment with acetic acid.

4. CONCLUSIONS

Cellulose can be successful isolated from banana fibres by treatment with acetic acid/ nitric acid. XRD patterns showed that the incorporation of $MgO.H_2O$ was effective. The FTIR analysis showed the partial acetylation of raw leaves of banana plant, with the decrease of hydroxyl groups. TGA curves show an increase of thermal stability compared to the cellulose for both hybrids. The incorporation of 2 wt% of the inorganic additive, $MgO.H_2O$, shown to be a viable alternative for hybridization of the cellulosic matrix as the decomposition temperature of major fraction of material occurred at much higher temperature (increase of 40 ^{o}C) than the cellulose decomposition. The materials that have been developed show potential as filler in polymer composite systems.

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