NOVEL CELLULOSE/$NbOPO_4.nH_2O$ HYBRID MATERIAL FROM SUGARCANE BAGASSE

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In recent years studies concerning the applications of lignocellulosic/ inorganic couples have resulted in the development of an interesting class of functional materials. In this work a cellulose/$NbOPO_4.nH_2O$ hybrid using cellulose from surgacane bagasse was prepared and characterized in order to test for adsorption applications. The preparation process was conducted by carrying out metallic niobium dilution in hydrofluoric acid in the presence of nitric acid, then adding boric acid to form the complex and, finally, the cellulose sugar cane bagasse was added. Concentrated phosphoric acid was also inserted to precipitate hydrous niobium phosphate particles in the cellulose fiber. This material was characterized by X-ray diffractometry (XRD), thermogravimetry (TG/DTG), and scanning electronic microscopy (SEM) connected to an energy dispersive spectrophotometer (EDS). Results by SEM/EDS show that $NbOPO_4.nH_2O$ was present in structure of the cellulose. During the preparation of the material, using boric acid it was observed that the formation of precipitate occurred in a shorter time than the material prepared without boric acid.

Keywords: Cellulose; Hybrid organic/inorganic; Hydrous niobium phosphate; Sugarcane bagasse

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INTRODUCTION

Sugarcane bagasse is an agro-industrial residue quite abundant in Brazil, comprised of cellulose, hemicellulose, lignin, and extractives. Cellulose is the most abundant organic chemical on earth. It is a glucan polymer of D-glucopyranose monomeric units, which are linked together by β-(1-4)-glucoside bonds. The building block for cellulose is actually cellobiose, since the repeating unit in cellulose is a two-sugar unit (Rowell 2005).

Hemicelluloses are polysaccharides composed of a number of different sugar units. The degree of polymerization (DP) of hemicellulose is of the order of 200 to 300, and in general it is less ordered than cellulose, although some can form crystalline units (Hill 2006).

Lignin is an amorphous, highly complex, phenolic polymer of indeterminate molecular weight that is considered to be an encrusting substance (Rowell 2005). Extractives are chemicals in the wood that can be extracted using solvents. During the process of separating the lignocellulosic fibers there are several treatments or processes contributing to purification. Alkaline treatments can remove impurities such as waxes, pectins, and mineral salts (Alvarez et al. 2006). Saheb and Jog (1999) reported the alkaline treatment of sugarcane bagasse to remove lignin and hemicelluloses.

Cellulose fibers are normally used in papermaking and textiles (Aracari and Vidal 2009), while its derivatives are used in plastics, paint, food, cosmetics, and various other such applications. Cellulose has been studied extensively as reinforcement due to its many intrinsic advantages, e.g. low cost, availability, renewability, biodegradability, low abrasivity, and easy handling (Tita et al. 2002). There are a great number of potential uses of cellulose within different industries. Recently, many studies on natural composite fibers have been carried out, such as with banana (Bilba et al. 2007), sisal (Silva et al. 2008), curauá (Spinacé et al. 2009), and sugarcane bagasse (Mulinari et al. 2009).

Composites employing sugarcane bagasse fibers have attracted an increasing interest in the scientific and industrial communities. The cellulose chemical modification from natural residues have been studied to meet various needs in the form of composites or membranes (Gushikem and Toledo 1999), fire retardants (Flambard et al. 2005), components for the automobile industry (Bodros et al. 2007), and polymer composites (Torres and Cubillas 2005; Albano et al. 2005; Luz et al. 2007; Sherely et al. 2008; Ly et al. 2008).

Organic-inorganic hybrid materials are of more than academic interest, since their inherent properties frequently lead to the development of innovative industrial applications. Such fields as electronics, optics, medicine, sensors, smart coatings, and polymer composites are some examples of promising application areas where these types of materials have been successfully applied (Sanchez et al. 2005).

Cellulosic fibers coated with metal oxides, Cell/M_xO_y, have been described and constitute an attractive new class of composite material (Da Silva et al. 1995; Padilha et al. 1995). Several metal oxides have been used for specific applications. These include porphyrin immobilization for use as an oxygen sensor (Campos and Gushiken 1997), TiO_2 for enzyme immobilization (Da Silva et al. 1996), Al_2O_3 coated cellulose fibers modified for adsorption (Alfaya and Gushikem 1999), Nb_2O_5 for cobalt(II), TiO_2 films on cellulose fibers (Uddin et al. 2007), and ZrO_2 for adsorption of sulphate ions (Mulinari and Da Silva 2008). In the most recent years considerable work has been reported on the preparation of nanocomposites based on natural cellulose (Marques et al. 2006; Gonçalves et al. 2008; Pinto et al. 2008, 2009; Gonçalves et al. 2009). The present work reflects the authors' interest in chemical products made from cellulose (Pereira 2010), aimed at producing materials with new functional properties with application in adsorption, to prepare membranes, for enzyme immobilization, and for reinforcement in polymers. Niobium phosphate has been used in selective adsorption of cetyl trimethylammonium bromide (CTAb) (Pereira 2009). On the other hand, less information exists about hydrous niobium phosphate coated cellulose. The material preparation was done using boric acid pre-formed fluorboro complex and phosphoric acid was carried to produce the Cell/$NbOPO_4.nH_2O$ hybrid in less time than without boric acid (Pereira 2010).

The objective of this paper is to demonstrate and explain the preparation of the cellulose/ $NbOPO_4.nH_2O$ hybrid using boric acid as a complexing agent, as well as its characterization by X-ray diffractometry (XRD), thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) connected to an energy dispersive spectrophometer (EDS).

EXPERIMENTAL

Materials

Unmodified cellulose

Unmodified sugarcane bagasse was pretreated with 10% sulfuric acid solution (in a 350 L reactor at 120 ºC and 10 min), followed by centrifugation with the purpose of separation of the rich pentosans solution. The extracted lignocellulosic fraction was delignified with a 1% NaOH solution (350L reactor at 100 ºC for 1 h).

Preparation of the bleached cellulose

The crude pulp obtained was bleached with acetic acid and sodium chloride with stirring and heating, followed by filtration under vacuum and exhaustive washing with distilled water. This technique was used to remove residual lignin. Furthermore the bleached cellulose was dried for 12 h at 50 ºC (Mulinari et al. 2006).

Preparation of the cellulose/hydrous niobium phosphate hybrid using boric acid

The preparation of hybrid Cell/ $NbOPO_4.nH_2O$ was similar to the procedure used by Pereira (2010) with some modifications. Hybrid was prepared by dissolving 3 g metallic niobium (product of the 4th fusion, produced in Demar, at EEL) in a acid mixture of HNO_3 (65%)/HF (40%) solution (1:3 molar). Afterwards 5 g of boric acid was added, resulting in a boric complex. Then 5 g cellulose in the form of bleached sugarcane bagasse was introduced to the solution, followed by concentrated orthophosphoric acid (50 mL, 85% w/w). The final mixture was heated in a steam bath until a crystalline precipitate formed after ca. 6 h. This suspension was treated with 120 mL of 5M nitric acid solution. The solid was washed with 60 mL distilled water and 60 mL ethyl alcohol solution. The product was then dried at 50 °C for 24h.

Characterization of the Materials

The hydrous niobium phosphate niobium, the bleached cellulose, and the hybrid Cell/$NbOPO_4.nH_2O$ prepared using boric acid were characterized by X-ray diffracttometry (XRD), thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) connected to an energy dispersive spectrophotometer (EDS).

X-Ray diffraction (RXD)

Crystallinity of the cellulose fibres was evaluated by X-ray diffraction using a Shimadzu diffractrometer model XRD6000. The measurement conditions were: CuKα radiation with graphite monochromator, 30 kV voltage and 40 mA electric current. The patterns were obtained in the range 10 to 70º, with a 2θ angular interval with 0.05º step and 1s of counting time. Results were expressed as the degree of crystallinity (*CI*).

Thermal analysis (TG/DTG)

TG/DTG was undertaken in order to understand the degradation characteristics of the hydrous niobium phosphate, the sugarcane bagasse cellulose, and the hybrid Cell/$NbOPO_4.nH_2O$ prepared with boric acid. TG curves were obtained by the use of a Shimadzu thermogravimetric instrument model TGA-50. Thermal behavior of the preparations was obtained by recording the TG/DTG curves between 25 and 900 ºC under conditions of nitrogen atmosphere using weighed samples in the range 5 to 10 mg at 20 ºC min^{-1}.

Thermal analysis (DSC)

The DSC analysis was performed using a calorimetric instrument DP Union, by the heat of the 5 mg sample at temperatures between 25 and 550°C, under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

Scanning electron microscopy (SEM)

A JEOL JSM5310 model scanning electron microscope (SEM) was used to observe the modification on cellulose fibres and hybrid. Samples to be observed under the SEM were mounted on conductive adhesive tape, sputter-coated with gold, and observed in the SEM using a voltage of 15 kV.

RESULTS AND DISCUSSION

In previous works made in our group (Tagliaferro et al. 2005) it was observed that the presence of HF did not permit the formation of a precipitate. Because of this, boric acid was added in the preparations. Its presence allows the formation of boron-fluorine complexes, eliminating then the excess of fluoride that exists in the solution, thus resulting in the formation of the wanted precipitate (Lee 1996).

Figure 1 shows the schematic reaction representation of the Lewis acid with the cellulose (Gushikem and Toledo 1999).

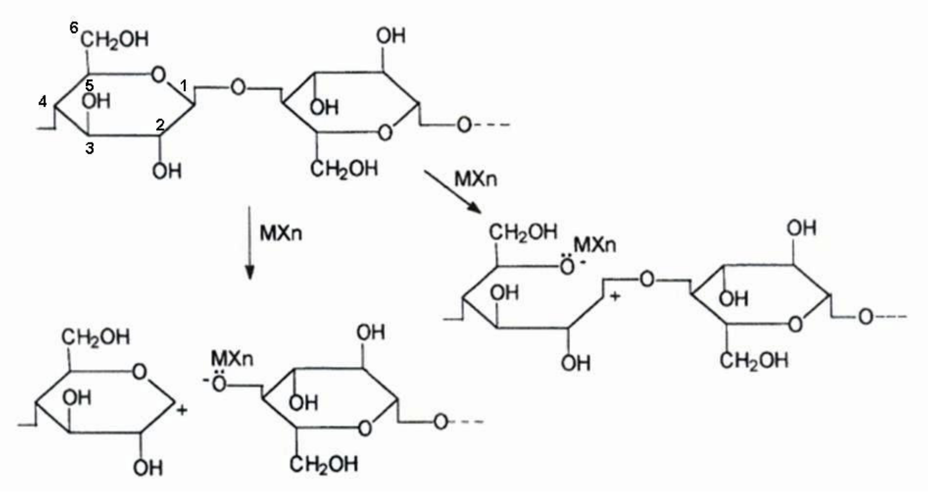


Fig. 1. Reaction of the Lewis acid with cellulose and formation of the donor-acceptor bond

If the organic-inorganic components are linked only by physicochemical interactions, namely dispersive van der Waals contributions, polar attractions, and/or hydrogen or ionic bonds, the materials are said to belong to class-I. In contrast, if the two phases are linked through covalent bonds, they pertain to class II (Cunha et al. 2010). In this case the hybrid was class I.

The XRD patterns of bleached cellulose, Cell/$NbOPO_4.nH_2O$ prepared with boric acid, and hydrous niobium phosphate are reported in Fig. 2.

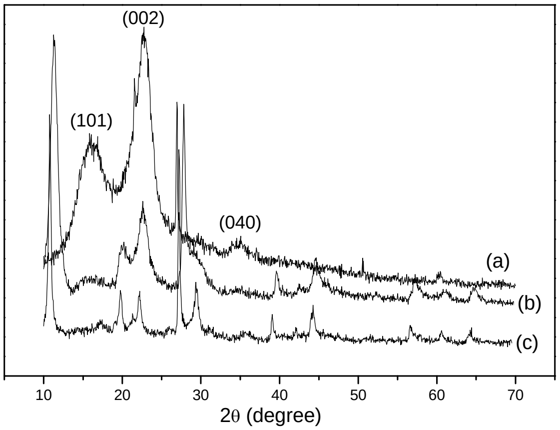


Fig. 2. X-ray diffractogram of bleached cellulose (a), Cell/$NbOPO_4.nH_2O$ prepared with boric acid (b), and hydrous niobium phosphate (c)

X-ray diffraction spectroscopy can be used to identify the material phases, to show materials with a regular and repetitive crystalline arrangement, and to present diffractograms having intense well-defined peaks and reflections.

According to D'Almeida, the X-ray diffractogram of cellulose shows that the fibers contain both crystalline (highly commanded) and amorphous (disordered) regions. Curve (2a) reports two broad peaks and one intense peak at 16° and 23°, respectively, which constitute the typical XRD pattern of cellulose fibers (Uddin et al. 2007). The hydrous niobium phosphate diffractogram (Fig. 2c) shows well-defined peaks corresponding to the crystalline regions.

Pereira et al. (2010) obtained curve C of Fig. 2. Using the values corresponding to this figure, the interplanar distances of the existing reflections were calculated and compared with the distances of JCPDS (Joint Committee on Podwer Diffraction Standards) patterns. The results did not correspond to any hydrated niobium phosphate catalogued. In this way, a thermal treatment was made in the materials at 600 ºC during 6 h, to remove existing water of hydration and to transform the material into $NbOPO_4$ form. The new interplanar distances calculated in the thermal treated materials corresponded to pure $NbOPO_4$. The JCPDS patterns, number 19-866, confirmed the presence of $NbOPO_4$.

In the same figure, we may observe that when the bleached cellulose was covered with hydrous niobium phosphate using boric acid (Fig. 2b), there was a change in the structure of the material, which is attributed to the crystalline character of the hydrous niobium phosphate.

Bleached cellulose (a), hybrid Cell/$NbOPO_4.nH_2O$ prepared with boric acid (b), and hydrous niobium phosphate (c) were evaluated by thermogravimetric analysis, and results are shown in Fig. 3. Many studies related to the decomposition of specific lignocellulosic materials can be found (Alvarez et al. 2006; Morán et al. 2008; Shen and Gu 2009).

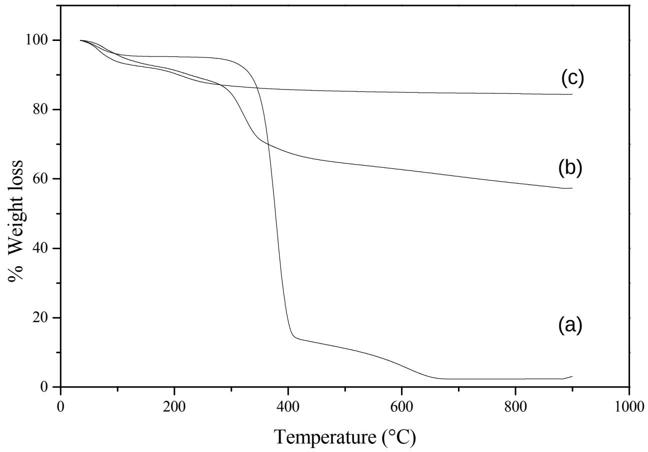


Fig. 3. Thermogravimetric curves: bleached cellulose (a), Cell/$NbOPO_4.nH_2O$ prepared with boric acid (b), and hydrous niobium phosphate (c)

Figure 3 shows the mass losses associated with bleached cellulose (a), hybrid Cell/$NbOPO_4.nH_2O$ prepared with boric acid (b), and hydrous niobium phosphate (c). A mass loss of 4.7%, 5.7%, and 7.1% between 40 and 150°C was observed for bleached cellulose, Cell/$NbOPO_4.nH_2O$ prepared with boric acid, and hydrous niobium phosphate, respectively, due to the evaporation of water from these samples (Martin et al. 2010; Bertoti et al. 2009; Li et al. 2009; Shaikh et al. 2009). For bleached cellulose (Fig. 3a) the results show two decompositions steps; between 200 and 500°C there was another high loss of mass (84%), followed by a second loss (8.6%), yielding residual char at 900 °C (Pereira and Da Silva 2010). On the other hand, the TG curve (Fig. 3b) of hybrid Cell/$NbOPO_4.nH_2O$ prepared with boric acid showed a second loss of mass between the temperature of 130 and 250 °C. This corresponded to the decomposition of the organic material. The third stage took place between 250 and 900°C, where degradation of material reached a maximum at 320 °C, leaving 38% residue. Based on the DTG peaks, it can be estimated that the interaction between organic and inorganic components contributed to a maximum speed of mass loss for $NbOPO_4.nH_2O$, cellulose and hybrid at 213°C, 378°C, and 320°C, respectively, between the temperatures of 170 and 600 °C. In the work done by Prado (2005), the amount of inorganic material deposited on the surface of the lignocellulosic material can be determined through residue amount by thermogravimetry. In the present research 38% of inorganic material was deposited on the surfaces. From this result, it is evident that the TG technique makes it possible to directly evaluate the amount of $NbOPO_4$ covering the cellulose fibers, as obtained by the synthesis procedure described before.

Figure 3c from the $NbOPO_4.nH_2O$ material exhibits degradation in two steps: the first occurred by elimination of water molecules weakly connected to the matrix, and the second occurred by elimination of water molecules that were more strongly connected material (Pereira and Da Silva 2009).

Curve b in Fig. 3 shows a progressive decrease in thermal stability in relation to bleached cellulose, which may be attributed to the presence of niobium phosphate on the surface, leading to a significant decrease in the thermal quality of the material.

The differential scanning calorimetry (DSC) technique was used to compare the thermal behavior of the bleached cellulose, hydrous niobium phosphate, and hybrid Cell/$NbOPO_4.nH_2O$ prepared with boric acid (b). Results are shown in Fig. 4.

The DSC curve of bleached cellulose (Fig. 4a) shows two endothermic peaks corresponding to enthalpies of dehydration and decomposition of cellulose (Fengel and Wegner 1989) respectively, in accordance with the analysis made in the present work. In all the thermograms from 25 to 130 °C an endothermic peak appeared due to evaporation of water (Shaikh et al. 2009). The DSC curve of the hybrid Cell/$NbOPO_4.nH_2O$ (Fig. 4b) prepared with boric acid shows three endothermic peaks, the first at 90 °C, the second at 204 °C, and the third at 300 °C, in which the first one is associated the removal of water and both the second and third are associated to decomposition of the material, which confirms TG results previously shown. The hydrous niobium phosphate showed two endothermic peaks at 132 and 238°C (Pereira and Da Silva 2009).

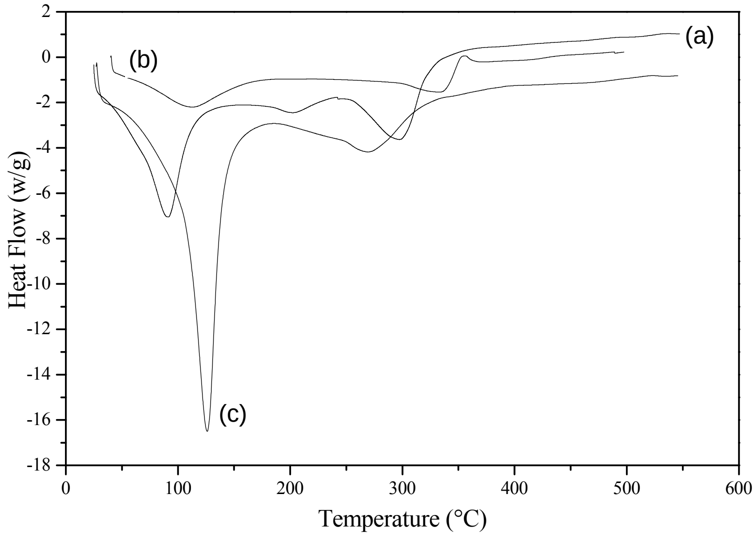
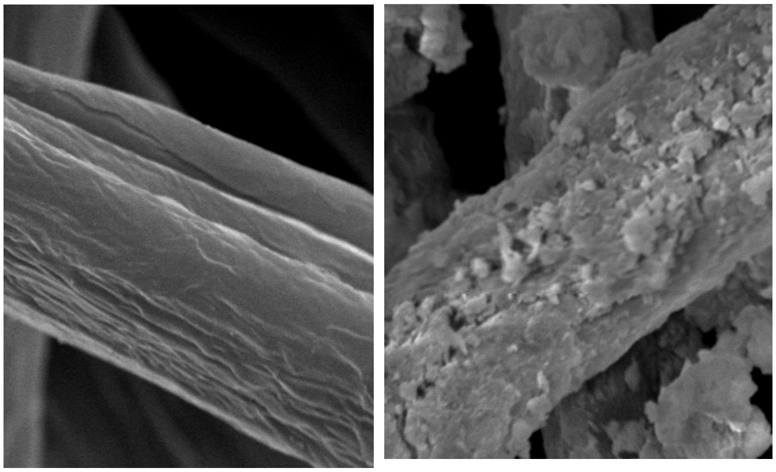


Fig. 4. DSC curves: bleached cellulose (a), Cell/$NbOPO_4.nH_2O$ prepared with boric acid (b), and hydrous niobium phosphate (c)

In order to investigate the morphology of the obtained samples, a comparison between the SEM images of the bleached cellulose and hybrid Cell/ $NbOPO_4.nH_2O$ is given in Fig. 5.



(a) 5000x (b) 5000x

Fig. 5. Scanning electron micrographs of bleached cellulose secondary electrons with 5000x (a), and Cell/$NbOPO_4.nH_2O$ prepared with boric acid with 5000x (b)

Figure 5a clearly shows the shape, fiber size distribution, and the roughness of the surface. It can also be observed that fibers had a flattened shape. Figure 5b shows hydrous niobium phosphate dispersed on the surface of the cellulose fibers. The hydrous niobium phosphate was deposited uniformly on the surface of the cellulose. Morphological changes were evident on the fiber surface, changing the overall appearance.

Energy dispersive spectroscopy (EDS) was also performed to verify the elemental composition of deposited materials on the fibers surface. Table 1 shows the relevant data for the hybrid Cell/ $NbOPO_4.nH_2O$. On the basis of these results, the deposited material comprised the elements, oxygen, phosphorus, and niobium. The element carbon can be attributed to the cellulose. This implies that $NbOPO_4$ particles were firmly anchored to the surface of fibres.

As is observed in Table 1, there was no fluorine or nitrogen in the material, which might have been expected due to the use of hydrofluoric/nitric acid in the preparation of the materials. It is seen that washing with water was sufficient.

Table 1. Compositions Obtained Using EDS

Element	**Materials prepared with boric acid (area 1)**		**Materials prepared with boric acid (area 2)**	
	wt%	at%	wt%	at%
C	36.27	24.51	34.82	23.55
Nb	56.68	51.03	58.37	58.37
O	3.56	6.21	3.36	5.85
P	3.41	18.25	3.45	18.02

CONCLUSIONS

The present method using boric acid to prepare the composite Cell/$NbOPO_4.nH_2O$ was very convenient and reproducible. Composite Cell/$NbOPO_4.nH_2O$ prepared by using boric acid as a complexion agent resulted in a speedy ability to obtain the material (6h), as well as dispersed particles on a cellulose surface. In the material preparation the formation of precipitate occurred in a shorter time than when compared to the preparation of the material using the conventional method. From scanning electron microscopy, changes in morphologies were observed. The niobium phosphate was non-homogeneously dispersed on the cellulose fiber surface. EDS analysis confirmed the presence of the elements niobium, phosphorus, and oxygen.

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