

STUDY OF THE PREPARATION, CHARACTERIZATION OF CELLULOSE/NIOBIUM PHOSPHATE COMPOSITE

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| Abstract

This article the preparation and the characterization of the cellulose/NbOPO₄.nH₂O composites using cellulose from surgacane bagasse was pesented. Composites were prepared using of metallic niobium dilution in a mixture of fluoridric/nitric (10:1) and after cellulose sugar cane bagasse was put addition into the solution and phosphoric acid added. These materials were characterized by X-ray diffractometry (XRD), thermogravimetry (TG/DTG), scanning eletronic microscopy (SEM) conected to a energy dispersive spectrophotometer (EDS) and differential scanning calorimetry (DSC). This article describes the preparation and characterization of the cellulose/NbOPO₄.nH₂O composites using cellulose from surgacane bagasse.

Keywords: *sugarcane bagasse, hydrous niobium phosphate, composites.*

INTRODUCTION

Composite inorganic/organic materials constitute an interesting new class of functional nanocomposite materials. These materials can show improved optical, thermal and mechanic properties, due to synergistic effects resulting from the physical or chemical interactions which occur between the inorganic and organic components (Romero, 2004).

Composites utilizing vegetable fibers have attracted increasing interest of the scientific communities. Cellulose is a readily available natural polymer which has been widely used as a substrate for reagent immobilization, having numerous applications, such as ion exchanges (Lederer, 1998), phosphate removal and organic pollutants (Thomas, 2005, Chung, 1998) and adsorption of dichromate ions (Mullinari, 2006), composite reinforced with cellulose from sugarcane bagasse (Luz, 2006, Gushikem, 2001), polymers composites (Campos, 1996; Da Silva, 1995; Alfaya, 1999, Lazarim, 2002), organic-inorganic composites (Campos, 1998), fire retardant (Gushikem, 1999; Borgo, 2002) and components for automobile industry, aeronautics and building site (Kurokawa, 1994; Gushikem, 2001).

The sugarcane bagasse is an agro-industry residue quite abundant in Brazil and its surplus can be in more than different applications.

Several processes and products have been reported that utilize sugarcane bagasse as a raw material (Padilha, 1995; Da Silva, 1996). A fibrous residue of cane stalks is obtained after the crushing and extraction of juice from the sugarcane. The sugarcane bagasse is a vegetable fiber mainly constituted by cellulose that is a glucose-polymer with relatively high modulus, often found as fibrillar component of many naturally occurring composites (wood, sugarcane straw and bagasse) in association with lignin (Campos, 1996).

The literature not reports the preparation of this type of composite using cellulose and niobium phosphate. However, cellulose fiber coated with metal oxides, Cell/ M_xO_y , has been described and constitutes an attractive new composite material (Campos, 1997; Padilha, 1995; Mullinari, 2006).

The objective of this work was prepared modified cellulose from sugarcane bagasse coated hydrous niobium phosphate. These materials were characterized by X-ray diffractometry (XRD), thermogravimetry (TG/DTG), differential scanning calorimetry (DSC) and scanning electronic microscopy (SEM) connected to a energy dispersive spectrophotometer (EDS).

EXPERIMENTAL

Preparation of the bleached cellulose

The bleached cellulose was obtained pretreated with 10% sulfuric acid solution (reactor of 350 L at 120°C, 10 min), followed by centrifugation with the purpose of separating the rich pentosanes solution. Extracted lignocellulosic fraction was deslignificated with 1% NaOH solution (reactor of 350 L at 100°C, 1 h) being obtained the crude pulpe and bleached with sodium chloride. Furthermore the bleached cellulose was dried in a store at 50°C, 12 h (Mullinari 2006).

Preparation of the cellulose /Hydrous Niobium Phosphate Composite

The materials cellulose hydrous niobium phosphate were prepared by dissolving 10 g of metallic niobium in mixture of fluoric/nitric acid (10:1,v/v). After the dissolution addition the bleached surgane bagasse cellulose. Then 100g of H₃PO₄ (40%) was added. The clear solution was heated on the water bath until a product precipitated, which was filtered. The product was washed with nitric acid, water and ethanol and air-dried at 50°C.

Characterization of the obtaneid materials

The materials were characterized by X-ray diffractometry (XRD), thermogravimetry (TG/DTG) scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

X-ray diffractograms were obtained in a Rich Seifert diffractometer model ISO- DEBYFEX1001. The following conditions were used to obtain the spectra: radiation CuK α , tension of 30 kV, current of 40 mA and 0.05 (2 θ /5 s) scanning from values of 2 θ it enters 10-70°C.

TG curves measurements were obtained in a Shimadzu thermogravimetric instrument model TGA-50. Thermal behavior for each one of the preparations was studied by recording the TG/DTG curves between 40-900°C rates under nitrogen atmosphere using weighted samples between 5-10 mg, at 20°C min⁻¹.

Micrographs were obtained in a scanning electron microscope Model JEOL JMS 5310 using low vacuum, in backscattered electrons for the cellulose and composites and secondary electrons. Samples were dispersed on a brass support and fixed with a double face 3M tape.

DSC curves were obtained in calorimetric instrument DP Union, heating 5mg the sample in the temperature between 25 -550°C, rates under nitrogen atmosphere reason of heating of 10°C min⁻¹.

RESULTS AND DISCUSSION

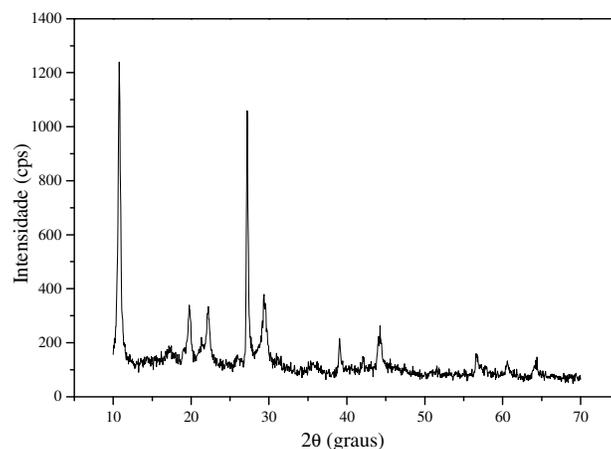


Figure 1. X-ray diffractogram of hydrous niobium phosphate.

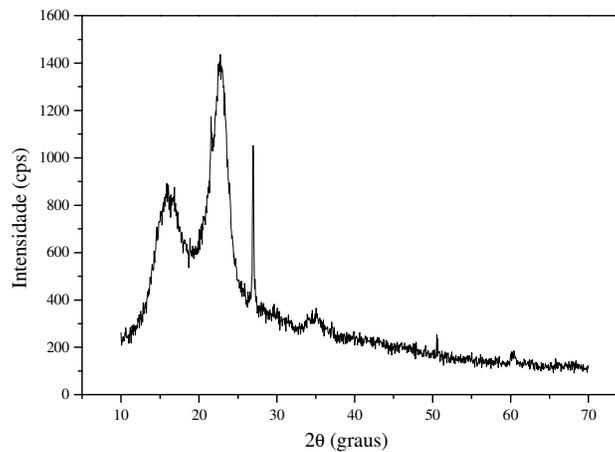


Figure 2. X-ray diffractogram of bleached cellulose.

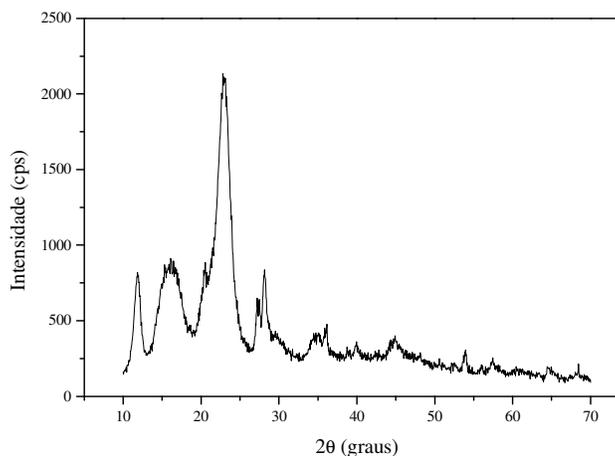


Figure 3. X-ray diffractogram of composite Cel/NbOPO₄.nH₂O.

The X-ray diffraction spectroscopy is a method the identification present phases in the material. These analysis , the materials with arrangement crystalline commanded and repetitive, they present diffractogram contend peaks and reflections well definite.

According to D` Almeida [1998], the X- ray diffractogram of the cellulose shows that the fibres corporate of crystalline regions (highly commanded) and amorphous (disordered). These regions do not possess well definite borders, but it seems to have transistion of an arrangement, in which these chains present a lesser orientation. In crystalline regions, the fibre has greater, resistance a traction, to the along and the solvation. It observes that when re-covering the bleached cellulose with hydrous niobium phosphate, it was gradual increase of the cristallinity in the composite (Figure

3) where compared with ray-X the bleached cellulose (Figure 2), which is attributed to the crystalline character of the hydrous niobium phosphate (Figure 1).

The analysis TG curves can also confirm the presence of hydrous niobium phosphate on the cellulose surface.

TG curves of the bleached cellulose, hydrous niobium phosphate and composite are presented in Figures 4, 5, 6.

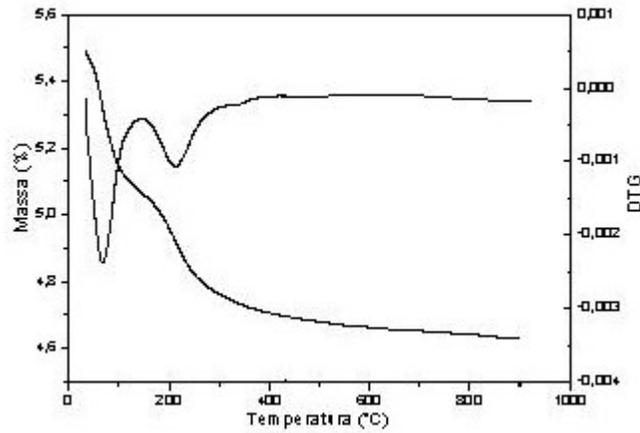


Figure 4. Curve TG/DTG of hydrous niobium phosphate.

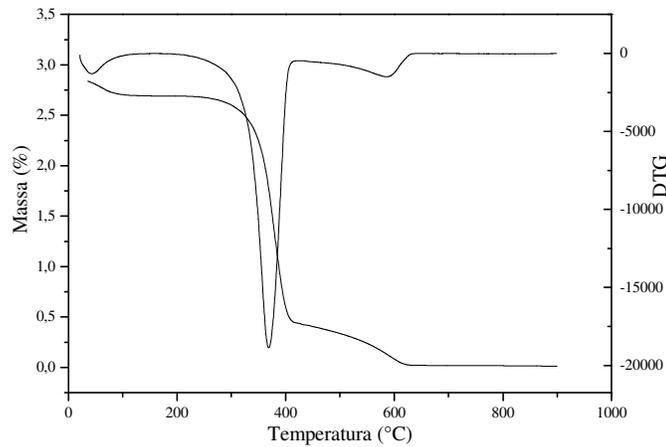


Figure 5. Curve TG/DTG of bleached cellulose.

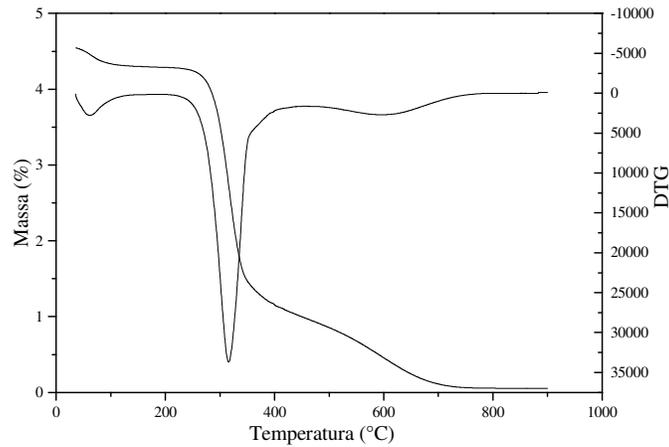


Figure 6. Curve TG/DTG of Cel/NbOPO₄.nH₂O composite.

The TG curve (Figure 4) of the hydrous niobium phosphate showed some loss mass occurring in two distinct stages within the temperature range of 25 to 550°C. In the first stages, between the temperature of 25 to 170°C, the losses have occurred by elimination of the water molecules weakly connected to the matrix, while in the second stage, between 170 and 550°C, it have occurred by elimination of the water molecules that were more strongly connected material. (Tagliaferro, 2005).

Table 1 shows the values of percentage of loss mass in the respective range of temperature, temperature of maximum mass loss obtained by differential curve (DTG) and residue occurred in the materials, with the data gotten by the TG curves (Figure 4, 5, 6).

Table 1. Results of TG curves of the materials, with the mass losses (m) in the respective range of temperature (ΔT), temperatures of maximum loss obtained by the differential curve (dm) and its respective residues (R).

Material	m (%)	ΔT (°C)	dm(°C)	R (%)
NbOPO ₄ .nH ₂ O	7,1	40-170	68	85,3
	7,6	170-550	213	
Cellulose	4.7	40-200	62	2.8
	84	200-500	378	
	8.6	500-800	613	
Cell/ NbOPO ₄ .nH ₂ O	5.7	40-200	64	11.5
	63.2	200-500	315	
	19.6	500-800		

It was observed that the percentage of residue in the composite (Table 1) it increased with respect the pure cellulose characterizing the present of material inorganic.

The Table 1 it can observe the presence of the inorganic in the $Cel/NbOPO_4 \cdot nH_2O$ desestabilized the composite, therefore in interval between 200 and 500°C, referring region the decomposition organic the material, it had decrease of the temperature (dm) of 378 to 315°C.

Comparing TG curves of the cellulose with of composite, was observed that the composite present a lesser mass loss in relation the cellulose, therefore the cellulose was practically all degraded while that the phosphate presented a 11,5% residue.

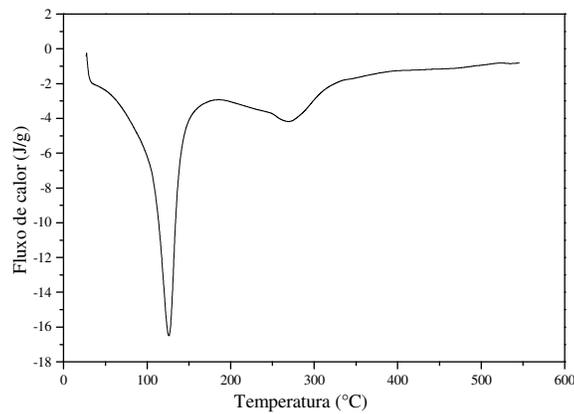


Figure 7. DSC curve of hydrous niobium phosphate.

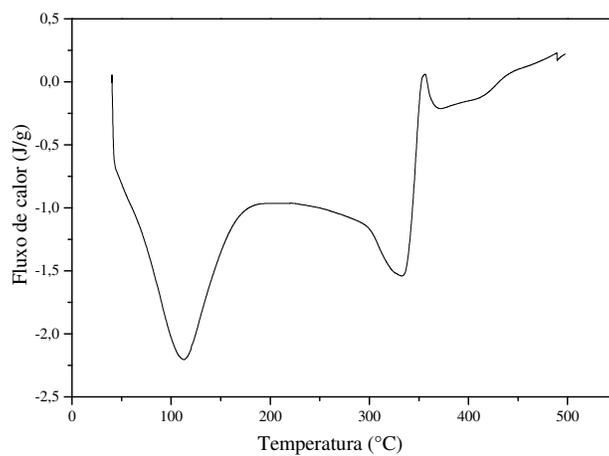


Figure 8. DSC curve of bleached cellulose.

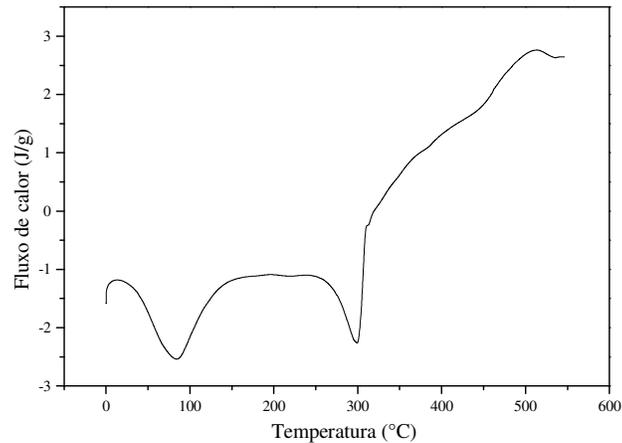


Figure 9. DSC do Compósito Cel/NbOPO₄.nH₂O.

The DSC curve the hydrous niobium phosphate (Figure 7) shows two peaks endothermic, the first in 131°C and the second in 238°C, both relative a enthalpy of dehydration of the material that occurring in two stages. In the first dehydration with $\Delta H_{des} = 235 \text{ J.g}^{-1}$, occurred by elimination of the water molecules weakly connected in matrix and the second dehydration com with $\Delta H_{des} = 44 \text{ J.g}^{-1}$, the second water molecules more strongly connected (Pereira, 2006). The DSC curve of bleached cellulose (Figure 8) shows two peaks endothermic that correspond the enthalpies of dehydration and decomposition of cellulose, respectively.

According to [Fengel and Wenger, 1989] the behavior DSC curve in relation the temperature of cellulose deriving of the wood shows two peaks endothermic in 126 and 325°C, respectively shows concordant with analysis made in the present work. The DSC curve of the composite (Figure 9) shows two peaks endothermic, the first in 84°C and the second in 300°C. In the first relative the dehydration and the second a dehydration/ decomposition of the material. Theses confirm the results gotten for TG.

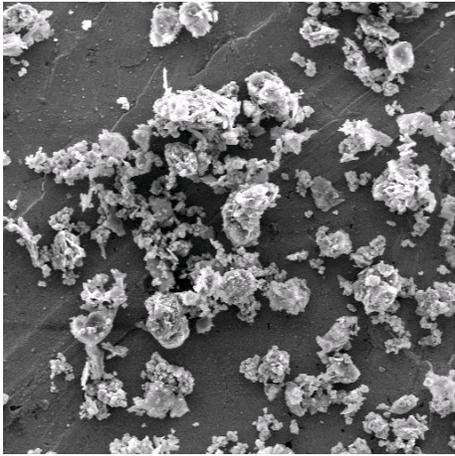


Figure 10. SEM micrograph of hydrous niobium phosphate 500X secondary electrons.

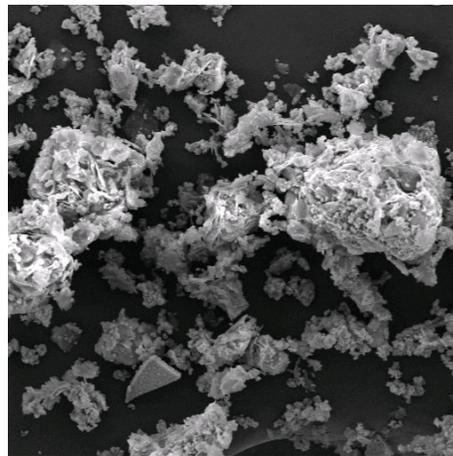


Figure 11. SEM micrograph of hydrous niobium phosphate 1000X backscattered electrons.



Figure 12. SEM micrograph bleached cellulose 500X secondary electrons.

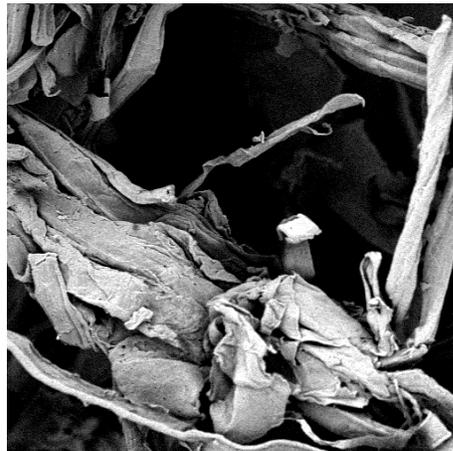


Figure 13. SEM micrograph bleached cellulose 5000X backscattered electrons.

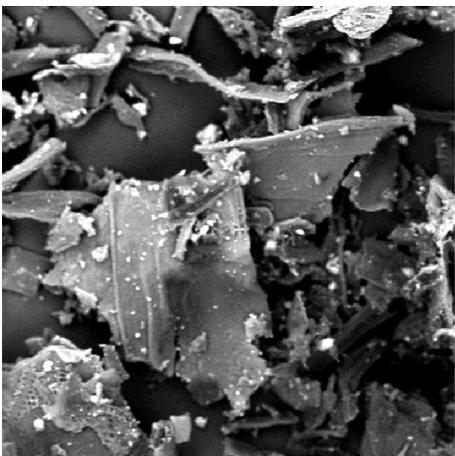


Figure 14. SEM micrograph Cel/NbOPO₄.nH₂O 500X secondary electrons.

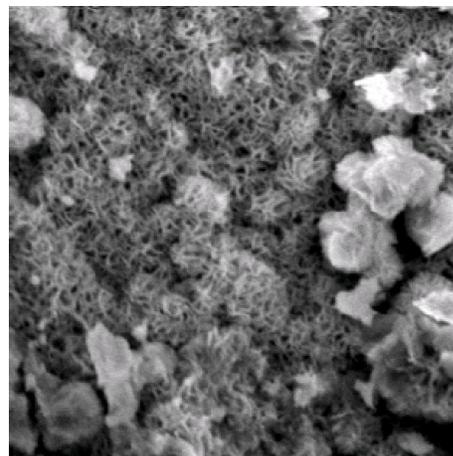


Figure 15. SEM micrograph Cel/NbOPO₄.nH₂O 5000X backscattered electrons.

The hydrous niobium phosphate (Figure 10 and 11) shows formed for great agglomerated and little porous blades.

The bleached cellulose micrograph (Figure 12 and 13) shows a great amount of fibers presents forms flattened and sizes. The Figure 14 and 15 shows the hydrous niobium phosphate dispersed on the surface of the fibers cellulose, however, it notices that the hydrous niobium phosphate was deposited not homogeneous form on the surface fibers cellulose. For the EDS analysis the presence of the elements niobium, phosphorus and oxygen can be confirmed.

CONCLUSION

The results show $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ are present in structure of the cellulose .

The X-ray diffractogram shows that the cell/ $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ has a lesser cristallinity than the pure cellulose, what confirm the presence of phosphate in the cellulose surface.

By EDS analysis the presence of the elements niobium, phosphorus and oxygen in composite was confirmed.

Scanning electron microscopy showed that the hydrous niobium phosphate particles wasn't homogeneously dispersed in the composite.

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