STUDY OF THE MECHANICAL PROPERTIES OF CELLULOSE CELLULOSE/ $ZrO_2.nH_2O$ NANOCOMPOSITES

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Abstract. *At present, the environment protection plays an important role when technologies development is a subject. In this work an alternative to the overload of sugarcane bagasse provided from the sugar and alcohol manufactures, relevant Brazilian cultures. Sugarcane fiber was processed in the milling and next the NaOH chemical treatment was conducted to provide lignocelullosic residues extraction. The fiber exposition to the hydrous zirconium oxide was conducted in pH 10 to reduce the zirconium producing the cellulose/hydrous zirconium oxide nanocomposite. The nanocomposite was characterized in tensile test and it was observed that the oxide layer on the cellulose promotes an increase in the strength of the material. It were conducted also scanning electron microscopy and thermogravimetric analysis.*

Keywords*: Cellulose fibers, nanocomposite, hydrous zirconium oxide.*

1. INTRODUCTION

Fibers when used as reinforcement in a polymeric matrix can improve the mechanical properties of the material if possess the modulus of elasticity higher than of the matrix. Main profits of mechanical properties send mainly how much to the modulus of elasticity and the resistance to the draining or rupture (Canevarolo, 2002).

Using bleached cellulose, after the removal of the lignocellulosic materials, the composite of this study will be prepared by the conventional precipitation method of oxide of zirconium provided of the zirconium oxychoride. The deposit of the metallic oxide in the surface of cellulose fibers could be proven through scanning electronic microscopy.

Cellulose and its derivatives are frequently used to prepare composite materials since present many intrinsic advantages, such as low cost, availability, biodegradability, and easy handling (Okamura, 1991). However, the polymer is relatively inert because hydrous groups, which are responsible for the majority of reactions with organic and inorganic reagents, are involved in inter and intramolecular hydrogen bonding (Koga, 1988). In recent years, many procedures for metal oxide-coated cellulose fibers preparation, Cell/ M_xO_y, have been described (Da Silva *et al.*, 1995; Padilha *et al.*, 1995; Sain *et al.*, 2002; Campos *et al.*, 1997). Depending on the nature of the metal oxide, have been used for specific applications: TiO_2 for enzyme immobilization (Da Silva *et al.*, 1996a), and retention and analysis of Cr(VI) (Da Silva *et al.*, 1996b), Al_2O_3 for immobilization of ion- exchange polymer (Alfaya *et al.*, 1999) and organofunctional groups for metal adsorption from ethanol solutions (Lazarin *et al.*, 2002), and Nb_2O_5 for cobalt(II) porphyrin immobilization and use as oxygen sensor (Campos *et al.*, 1998).

The experimental methodology of the fiber-coating process depends on which of the cellulose process is conduct: as fiber or as membrane. In the fiber form, the treatment of cellulose with a precursor reagent can be made in aqueous or non-aqueous solvent. To prepare the membranes, cellulose acetate is normally used due to its very soluble characteristics in most of the common organic solvents (Gushikem *et al.*, 1999).

Generally, two procedures are also used to coat fibers in the membrane form: (a) Acetate cellulose and precursor reagents are dissolved in a non-aqueous solvent, molded as a membrane, and followed by the phase-inversion process and (b) the previously prepared membrane is immersed in a solution of the precursor reagent followed by its hydrolysis (Borgo *et al.*, 2002).

Oxides structural transformations are related to the form as interact with the cellulose. Gushikem and Da Silva (2001) affirm that the interaction of the zirconium occurs by means of hydroxyl groups of the cellulose, which attribute to a character covalent.

In this work some adaptations will be made to describe the method of literature, that was called conventional precipitation (PC) in which, the precipitated (ammoniac solution) is added to an acid solution of the zirconium oxychloride, producing hydrous zirconium oxide.

Some techniques of analyses supply information about the modified materials as well as the pure materials. The morphology of dispersed metallic oxide on the cellulose can be studied by x-ray diffractometry (XRD) and scanning electron microscopy (SEM). The thermal stability of the composites can be studied by thermogravimetry (TG/ DTG) to determine the loss mass in a certain interval of temperature.

The objective of this work is prepare and characterize modified cellulose from sugarcane bagasse coated with hydrous zirconium oxide, since this residue have been used as fiber reinforce of polymer matrix, it is possible use the composite in structural application (Pandey *et al.*, 2000; Sene *et al.*, 2002; Adsul *et al.*, 2004).

There are several methods for characterization of cellulose fibers and cellulose/hydrous zirconium oxide composites, in this work we describe the preparation and characterization these materials by X-ray diffractometry, thermogravimetrics analysis, scanning electron microscopy and tensile tests.

2. EXPERIMENTAL

2.1 . Preparation of the bleached cellulose

The bleached cellulose was obtained by the following way: the sugarcane bagasse was pretreated with 10% sulfuric acid solution (reactor of 350 L at 120 ºC, 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 ºC, 1 hour) being obtained the crude pulpe and bleached with sodium chloride and then the bleached cellulose dry in a stove at 50 ºC, 12 hours (Rocha, 2000).

2.2. Preparation of the Hydrous Zirconium Oxide by Conventional Precipitation Method (PC)

Five grams of zirconium oxychloride were dissolved in 100 mL of aqueous hydrochloric acid solution (0.5 $mol.L^{-1}$). The precipitate was obtained adding an ammonium solution (1:3) at pH 10.0, under stirring, which was filtered , rinsed several times with distilled water for the complete removal of chloride ions (negative silver nitrate test). Finally, the product was dried at 50 ºC for 20 hours.

2.3. Preparation of the Cellulose/ Hydrous Zirconium Oxide Composite by Conventional Precipitation Method (PC)

Two grams of zirconium oxychloride were dissolved in 100 mL of aqueous hydrochloric acid solution (0.5 $mol.L^{-1}$) and mixed with 5 g of bleached cellulose. This material was precipitate with ammonium solution (1:3) at pH 10.0 and under stirring. The solid was filtered under vaccum, rinsed several times in distilled water for the complete removal of chloride ions (negative test to silver nitrate). The product was dried at 50 ºC for 24 hours. The resulting composite was designated as Cell/ $ZrO_2.nH_2O$ (2 g) PC.

2.4. Characterization of materials

Prepared materials were characterized by x-ray diffractometry (XRD), scanning electron microscopy (SEM), tensile test and thermogravimetric analysis.

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

The prepared materials were characterized by thermogravimetry (TG/ DTG) using a Shimadzu thermogravimetric instrument model TGA-50. Thermal behavior for each one of the preparations was studied by recording the TG and DTG curves between 40 to 800 ºC under nitrogen atmosphere using weighted samples between 5 to 10 mg.

Micrographs were obtained with a scanning electron microscope LEO1450V using low vacuum, in backscattered electrons for the cellulose and composites and secondary electrons for oxide. Samples were dispersed on a brass support and fixed with a double face 3M tape.

3. RESULTS

3.1. X-Ray Diffractograms

The hydrous zirconium oxide incorporated on the cellulose surface can be seen through the analysis XDR. The x-ray diffractogram of the cellulose shows characteristics of crystalline material, with intense peak (Fig. 1A). Instead of the hydrous zirconium oxide x-ray diffactogram shows characteristics amorphous material, without defined peaks (Fig. 1B). As expected, it was observed that coating cellulose with hydrous zirconium oxide, presents a gradual reduction of the cristallinily, which is attributed to the amorphous character of the hydrous zirconium oxide (Fig. 1C).

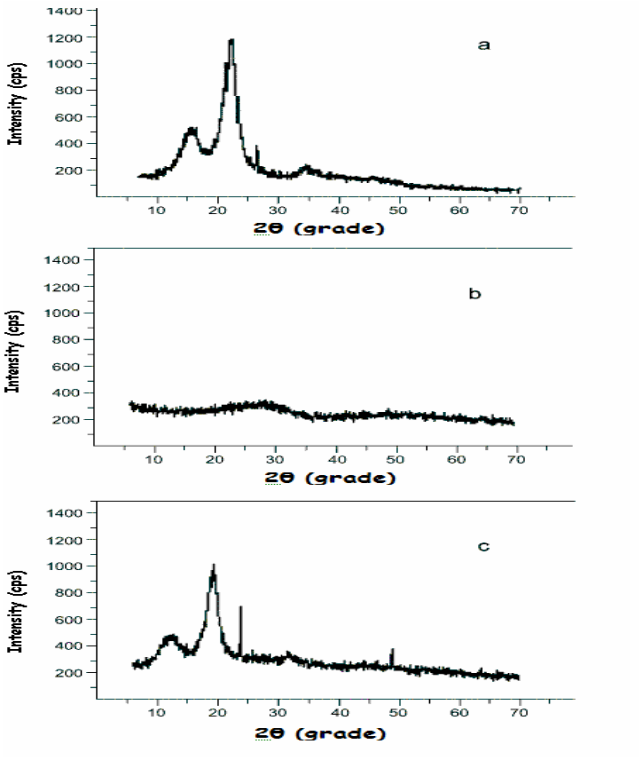

Figure 1. X-ray: (A) Bleached cellulose; (B) $ZrO_2.nH_2O$; (C) Cell/ $ZrO_2.nH_2O$ (2g).

These results were confirmed by scanning electron microscope (SEM).

3.2. Scanning Electron Microscopy

The bleached cellulose micrograph (Fig. 2A) shows a great amount of fibers which present flattened forms, while the hydrous zirconium oxide (Fig. 2B) presents as a little porous agglomerate. Figures 2C and 2D show the hydrous zirconium oxide dispersed on the surface of the cellulose fibers, however, it notices that the oxide was not deposited on uniform form on the cellulose fibers surface.

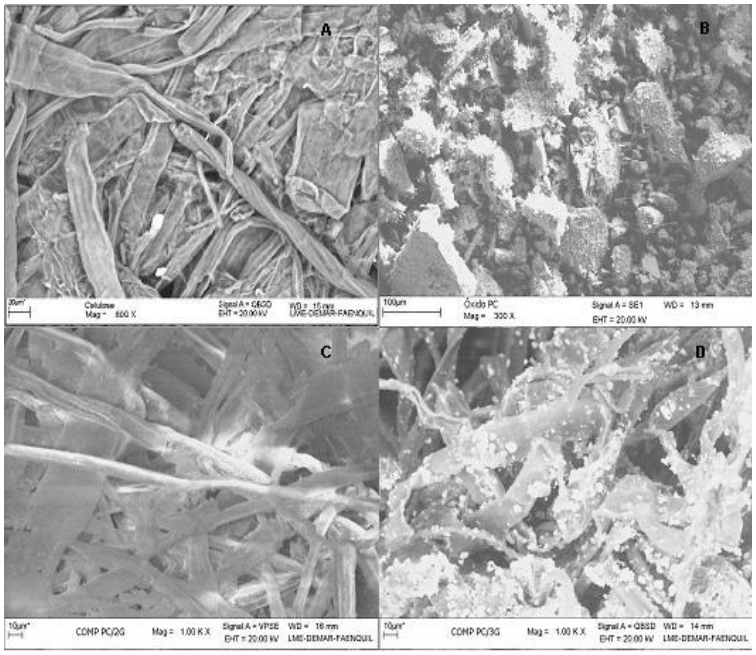

Figure 2. Micrographs: (A) Bleached cellulose; (B) $ZrO_2.nH_2O$; (C e D) Cell/ $ZrO_2.nH_2O$.

3.3. Tensile Test

Four assays of traction in the confectioned bodies of test from the cellulose had been carried through.

The traction assays (Tab. 1) had shown a low tensile strength. These data will serve as parameter for future analyses when the fiber to serve of reinforcement in composites with diverse polymeric matrices.

Table 1. Tensile strength

Material	Tensile Strength (MPa)
Cellulose	0,98 ± 0,22

The gotten assays had supplied when comparative well low values with other staple fibers. However, the way as they had been gotten the body-of-test may indicate the causes of the imperfection when no matrix was added.

3.4. Thermogravimetric Analysis

The thermogravimetry (TG/DTG) was used to verify the thermal stability of the composites, oxides and the cellulose, as well as the amount of deposited material.

The thermogravimetric curve of the cellulose presents a bigger loss of mass in relation to the composites in the temperature interval between 200-500ºC.

The residue of each composite mentions the amount to it of oxide, which was not degraded.

Table 2 shows the percentage of loss of mass and residue occurred in the composites.

Comparing the thermogravimetric curve of the cellulose with the oxides, the latter present a lower loss of mass in relation to the former, therefore the cellulose was practically all degraded while the oxide presented a 71% residue.

Table 2. Results obtained by means TG/DTG curves.

Material	Corresponding Temperature to the maximum of loss in curve DTG (ºC)	Interval (ºC)	Loss mass in TG curve (%)	Residue (%)
Cellulose	62,16 377,57 612,57	40 – 200 200 – 500 500 – 800	4,73 83,92 8,62 ∑ = 97,27	2,73
$ZrO_2.nH_2O$	114,48	40 – 500 500 – 800	28,29 0,58 ∑ = 28,87	71,13
Cell/ $ZrO_2.nH_2O$	61,72 337,53	40 – 200 200 - 500 500 – 800	7,12 77,73 2,93 ∑ = 87,78	12,22

Table 3 shows the percentages of $ZrO_2.nH_2O$ deposited in the cellulose, whose values had been extracted from thermogravimetrics curves. Being that the lost mass corresponds to the interval of 200-300ºC, or either, where it had greater loss of mass.

Table 3. Percentage grafted material.

Material	Initial Mass (mg)	Loss Mass (mg)	Final Mass (mg)	Grafted Material (%)
Cell/ $ZrO_2.nH_2O$ (2 g) PC	4,195	3,261	0,934	28,6

4. CONCLUSION

The scanning electron microscope (SEM) showed a good dispersion on the surface of the fibers for $ZrO_2.nH_2O$.

The X-ray diffractogram shows that the Cell/ $ZrO_2.nH_2O$ has a lower cristallinity than the pure cellulose, confirming the presence of oxide in the cellulose surface.

We can say that the conventional precipitation method (PC) is a good one to prepare and that these materials can be used as reinforcing fibers in polymer matrix.

The tensile test showed low resistance without the are no matrix and no oxide within the fiber.

5. REFERENCES

Adsul M.G., Ghuli J.E., Singh R., Shaikh H., Bastawde K.B., Gokhale D.V., Varma A.J., 2004, "Polysaccharides from bagasse: applications in cellulose and xylanase production", Carbohydrate Polymers, Vol. 57, pp. 67-72.

Alfaya R.V.S., Gushikem Y., 1999, "Aluminum oxide coated cellulose fibers modified with n-propyl chloride silsesquioxane polymer: preparation, characterization and adsorption of some metal halides from ethanol solution", Journal of Colloidal and Interface Vol.213, pp. 438-444.

Borgo C.A., Gushikem Y., 2002, "Zirconium phosphate dispersed on a cellulose fiber surface: preparation, characterization, and selective adsorption of Li^+, Na^+ and K^+ from aqueous solution", Journal of Colloid and Interface Science, Vol. 246, pp. 343-347.

Campos E.A., Gushikem Y., 1997, "Composite membrane of niobium(V) oxide and cellulose acetate: preparation and characterization", Journal of Colloid and Interface Science, Vol. 193, pp. 121-126.

Campos Y.G.A., Gushikem Y., 1998, "Cobal(II) hematoporphyrin IX immobilized in a cellulose acetate niobium(V) oxide composite membrane: preparation and oxygen reduction study". Journal of Brazilian Chemical Society, Vol. 9, pp. 273-278.

Canevarolo Jr., S.V., 2002, "Ciência dos Polímeros", Ed. Artliber, São Paulo, Brasil, p.161.

Da Silva L.R.D., Filho U.P.R., Gushikem Y., Gonçalves M.C., Castro S.C., 1995, "Highly dispersed titanium (IV) oxide on α- cellulose surface: an XPS, SEM, and XRD study", Journal of Applied Polymer Science Vol. 58, pp. 1669-1673.

Da Silva L.R.D., Gushikem Y., Kubota L.T., 1996a "Horseradish peroxidase enzyme immobilized on titanium(iv) oxide coated cellulose microfibers: study of the enzymatic activity by flow injection system" Colloids and Surfaces B. Biointerfaces Vol. 4, pp. 309-315.

Da Silva L.R.D., Peixoto C.R.M., Gushikem Y., Kubota L.T., 1996b. "Use of alpha-cellulose coated with titanium(IV) oxide in separation of Cr(VI)", Separation Science and Technology, Vol. 31, pp. 1045-1057.

Gushikem Y., Da Silva L.R.D., 2001, "Study of the cellulose influence on the titanium hidroxide crystallization by calcination process", Anais Assoc. Bras. Química Vol. 50, pp. 166-170.

Gushikem Y.; Toledo E.A., 1999, "Preparation of Coated Cellulosic Fiber", Ed. Marcel Dekker, USA, 13, p.509.

Koga M.E.T., 1988, "Celulose e Papel: Tecnologia de Fabricação da Pasta Celulósica", 2ª ed., IPT /SENAI, São Paulo, Brasil, p.50.

Lazarin A.M., Gushikem Y., 2002, "Nitrogen containing organosilicon bonded an Al_2O_3 – cellulose acetate hybrid material: preparation, characterization and use for adsorption of Fe(III), Cu(II) and Zn(II) from ethanol solutions", Journal of Brazilian Chemical Society, Vol. 71, pp. 88-94.

Okamura K., 1991, "Structures of cellulose", Ed. Marcel Dekker, Nova York, p. 67.

Padilha P.M., Campos J.T.S., Moreira J.C., Federici C.C., 1995, "Estudo das propriedades de troca iônica e/ou da celulose e celuloses modificadas", Química Nova, Vol. 18, pp. 529-533.

Pandey A., Soccol C.R., Nigam P., Soccol V.T., 2000, "Biotechnological potential of agro-industrial residues: sugarcane bagasse", Bioresource Technology Vol. 74, pp. 69-80.

Rocha, G.J.M., 2000, "Deslignificação de Bagaço de Cana de Açúcar Assistida por Oxigênio", Tese de Doutorado, Universidade Federal de São Carlos.

Rodrigues U.P.J., Cachichi R.C., Gushikem Y., Gonçalves M.C., Castro S.C., 1996, "Composite membranes of cellulose acetate and zirconium (IV) oxide: preparation and study of physicochemical characteristics", Chemistry Materials, Vol. 8, pp. 1375- 1379.

Sain M., Boucher J., 2002, "Characterization and properties of lignocellulosic fibers with thin-film deposited cationic precursor", Colloids and Surfaces, Vol. 196, pp. 97-109.

Sene L., Converti A., Felipi M.G.A., Zilli M., 2002, "Sugarcane bagasse as alternative packing material for biofiltration of benzene polluted gaseous streams: a preliminary study", Bioresource Technology, Vol. 83, pp. 153-157.

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