DEPOSITION OF SIO_2 NANOPARTICLES ON CELLULOSE FIBERS FOR DECREASING THEIR WATER ABSORPTION IN FIBER-CEMENT

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ABSTRACT

One of the drawbacks in the use of cellulose fibers in fiber-cement products is their high water absorption, which leads to fiber mineralization in the Portland cement matrix. Thus, this study aimed to evaluate different reaction conditions for deposition of the SiO2 nanoparticles on the surface of cellulose pulp fibers, and their influence on the moisture adsorption of the hybrid organic-inorganic material formed. SiO2 nanoparticle deposition was done with the sol-gel process, testing four reaction times (2, 12, 18 and 24 h) and three contents (1.00, 2.25 and 4.50 mL) of the tetraethyl orthosilicate (TEOS) precursor. The modification time and TEOS precursor content directly influence the amount of Si deposited on the fiber surface, the nanoparticle diameter distribution, and the resistance to moisture adsorption. The moisture adsorption capacity of the modified cellulose fibers was reduced up to 50%. These results are interesting for ongoing research in the direction of fiber modification strategies for application of the cellulose fibers as durable reinforcement in cement based composites.

KEYWORDS:

Vegetable fibers; silica nanoparticles; moisture adsorption; cement based materials.

INTRODUCTION

Lignocellulosic materials and kraft pulp fibers have being increasingly used as reinforcement in cement-based materials in low cost construction materials in most developing countries (Adefisan, 2011; Marzuki et al., 2011; Mendes et al., 2011; Tonoli et al., 2011). Among kraft pulps, bleached Eucalyptus kraft pulp is the most abundant and has becoming increasingly more available than others. Fiber-cement products had been widely used in the world as corrugated or flat roofing materials, cladding panels and water containers, in a large number of building and agriculture applications (Ikai et al., 2010; Tonoli et al., 2010a). The main reason for incorporating fibers into the cement matrix is to improve the toughness, tensile strength, and the cracking deformation of the composite. Another reason for using fibers is due to their capacity of solids retention during processing of the composites produced by the Hatschek process, which is the most widely employed one in producing fibre-cement components (Dias et al., 2010).

One of the drawbacks in the use of cellulose fibers in fiber-cement products is their high water absorption, which leads to their mineralization in the high alkali Portland cement matrix, with the pH around 13. Mineralization of the cellulose fibers is caused by the free ions from the dissolution of Portland cement phases

that penetrated into the fiber cavity (lumen), leading to the re-precipitation of ettringite/monosulphate and calcium hydroxide into the fiber. This re-precipitation of solids into the fiber voids induces the stiffening of the cellulose fibers. Hence, the optimal situation would be to protect the cellulose fibers from mineralization with a less aggressive matrix (e.g. lower alkalinity), maintaining the fiber strength and the quality of the fiber bridging that guarantee composite ductility. Thus, this study aimed to evaluate different reaction conditions for deposition of the SiO2 nanoparticles on the surface of cellulose pulp fibers, and their influence on the moisture adsorption of the hybrid organic-inorganic material formed.

METHODOLOGY

Material

Eucalyptus (Eucalyptus urophyla x Eucalyptus grandis) cellulose fibers were obtained from the commercial kraft pulping process, with average fiber length of 0.81±0.01 mm and average width of 15.9±0.3 μm. Chemical composition of the fibers was cellulose (86.3%), hemicelluloses (12.9%), ashes and extractives (0.8%).

Chemicals include the inorganic SiO_2 precursor tetraethyl orthosilicate ($C_8H_{20}O_4Si$ – TEOS, 98%), the synthesis catalyst ammonium hydroxide (NH_4OH – 30% $v.v^{-1}$), the ethanol solvent (CH_3CH_2OH – 95% P.A.), and the potassium sulfate (K_2SO_4) used for humidity control in the moisture adsorption test.

Deposition of the SiO_2 nanoparticles on the cellulose fibers

Cellulose fibers were kept in deionized water under mechanical stirring for 24 h in order to achieve total disintegration of the cellulose pulp sheets and proper fiber dispersion. Water to fiber consistency for this dispersion was 100 $mL.g^{-1}$.

Modification of the cellulose fibers with the deposition of the SiO_2 nanoparticles was carried out by the sol-gel process, based on previous studies (Pinto et al., 2008; Ashori et al., 2012). 0.5 g of cellulose fibers was immersed in a solution composed of 42.5 mL of ethanol, 4.5 mL of deionized water, and 0.75 mL of ammonium hydroxide. Constant and moderate mechanical stirring (300 rpm) was kept for 2 h, after which TEOS solution was slowly added, drop-by-drop, and a solution with fiber consistency of 100 $mL.g^{-1}$ was achieved. Four reaction times (2, 12, 18 and 24 h) and three TEOS contents (1.9, 4.2 and 8.4 g of TEOS per g of cellulose pulp fiber) were tested, as presented in Table 1. All modifications were performed at room conditions (around 25 ºC and 70% RH).

Table 1. Fiber modification conditions.

Samples	Time of reaction (h)	TEOS content ($g.g^{-1}$)
Control	-	-
$T_2C_{1.9}$	2	1.9
$T_2C_{4.2}$		4.2
$T_2C_{8.4}$		8.4
$T_{12}C_{1.9}$	12	1.9
$T_{12}C_{4.2}$		4.2

$T_{12}C_{8.4}$		8.4
$T_{18}C_{1.9}$		1.9
$T_{18}C_{4.2}$	18	4.2
$T_{18}C_{8.4}$		8.4
$T_{24}C_{1.9}$		1.9
$T_{24}C_{4.2}$	24	4.2
$T_{24}C_{8.4}$		8.4

The resultant modified fibers were vacuum filtered and thoroughly washed with deionized water until the filtered water becomes clean. The modified fibers were conditioned between filter paper sheets and kept in a desiccator for 24 h. Afterwards, the modified fibers were pressed under 3.3 MPa for 5 min in order to obtain a fiber sheet with flat surface. The fiber sheets were dried at 60 ºC for 48 h before characterization.

Scanning electron microscopy (SEM)

Morphological characteristics of the fibers were evaluated by SEM micrographs in a JEOL JSM-6510 microscope with a tungsten filament operating at 15 kV. An energy dispersive spectroscopy (EDS) system (model JEOL 6742A - Ultradry Silicon Drift) with an active area of 10 mm^2 and 132 eV resolution was used to detect and semi-quantification of SiO_2 particles at the fiber surface. Average percentage of Si (% by mass) was obtained after five scans per sample in a 1 μm^2 area. The fiber samples were bonded over a carbon tape on the metallic stubs and carbon coated (for EDS measurements) and gold coated (for MEV observations) before analyses.

Measurements of the SiO_2 nanoparticle diameters were performed using the Image J software, as reported in Mori et al. (2014). About 100 measurements were made for each condition in the SEM representative images, in order to obtain the diameter distribution of the nanoparticles at the cellulose fiber surface.

Moisture adsorption analysis

Three samples of each modification condition (2.0x1.0x0.1 cm) were pre-dried overnight at 105 ºC, weighted and placed in hermetically closed containers with 97±2% of relative humidity (RH) and 20±2 ºC, using a saturated potassium sulfate solution, as prescribed by the ASTM E104 (2012) standard. The moisture adsorbed by the samples along the time was determined by weighting (0.0001 g precision) them at successive intervals until they reached a constant weight. The amount of moisture adsorbed (MA) by the samples was calculated as follows (Eq. 1):

$$MA(\%) = [(Mt-M0)/M0]x100 \quad (1)$$

Where, M0 and Mt are the initial mass of the sample (prior to exposure to moisture) and the sample mass after t hours of exposure to moisture (97±2% RH), respectively. Each data point represents an average of three samples.

RESULTS AND DISCUSSION

Morphology of the SiO_2 nanoparticles on the cellulose fibers

Raw cellulose fibers presented smooth and uniform surface, basically comprised of carbon (C) and oxygen (O), with small and negligible amounts of sodium (Na), aluminum (Al) and silicon (Si) and a characteristic Si peak (Figure 1a).

SEM and EDS analyses of the modified fibers (Figure 1b) show the SiO_2 nanoparticles deposited on the fiber surface, as observed by the increase of the Si peak in the EDS measurement, which proves the effective modification with SiO_2 nanoparticles well dispersed at the fiber surface. This SiO_2 deposition is caused by the hydrolysis of the TEOS precursor and subsequent condensation of the resultant hydroxyls groups on the surface of the fibers (Xie et al., 2009; Tripathi and Shahi, 2011). Although no information was available from EDS measurements about the thickness or degree of SiO_2 covering, the results strongly suggest that a hybrid cellulose+SiO_2 composite was formed since Si peak was remarkably intense in relation to C and O peaks (Tonoli et al., 2009). Other studies showed successful modification of cellulose fibers with TEOS precursor by the sol-gel process. Properties achieved include reduction on water uptake and improvement of mechanical strength due to strong chemical interactions between cellulose and silica phases (Ashori et al., 2012; Pinto et al., 2008). On the other hand, further studies are needed to verify if the high silica content on the modified fibers causes excessive tool wear during processing. For example, Researchers reported concerns on this matter for application of bamboo as composite lumber (Malanit et al., 2007), black locus wood species for particleboard production (Nemli et al., 2004), and rice and bamboo for MDF production (Hiziroglu et al., 2007).

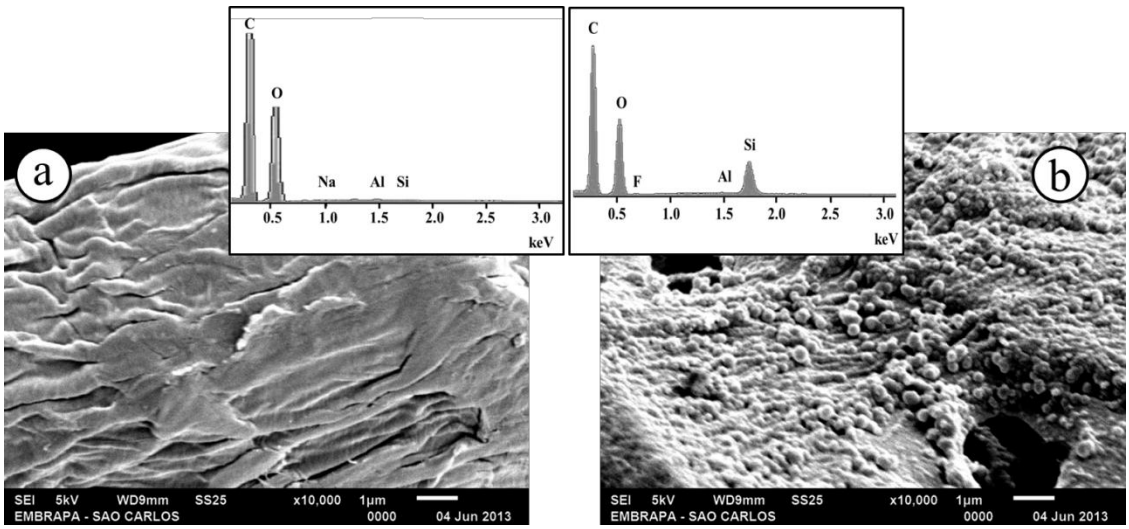

Figure 1. SEM images and EDS measurements of: (a) unmodified and (b) modified cellulose fibers ($T_{12}C_{4.2}$).

SEM micrographs of the modified fibers were analyzed using the "Image J" software in order to investigate the diameter of the SiO_2 particles deposited on the fiber surface (Table 2). Average particle diameter was over 100 nm for all modification conditions. The lowest (131±37 nm) and highest values (271±52 nm) were found

for $T_{12}C_{1.9}$ and $T_{24}C_{4.2}$, respectively. Except for the time of 12 h, the concentration of 4.2 $g.g^{-1}$ of TEOS resulted in the higher diameter values of the particles. The increase in the particle diameter with the increase of reaction time was observed for all TEOS contents; hence the results assure that variations in this parameter are clearly relevant.

Table 2. Average diameter (in nm) and standard deviation of the SiO_2 particles deposited on the fiber surface.

Conditions	$C_{1.9}$	$C_{4.2}$	$C_{8.4}$
T_2	149± 35	160±58	147±49
T_{12}	131±37	166±55	178±50
T_{18}	158±35	192±45	147±47
T_{24}	165±54	271±52	161±45

Bleached cellulose fibers are more susceptible to mineralization, because extractives, lignin, hemicelluloses and pectins are removed, which acts as a chemical and physical barrier to the penetration of Ca ions into the fibers (Tonoli et al., 2010b). Mohr et al. (2006) also reported that lignin and wood extractives play a protecting role against fibre mineralization. Therefore, the deposition of SiO_2 particles on the surface of bleached fibers may exert the same protective role of lignin against fiber mineralization.

Moisture adsorption

Most samples had their mass gain stabilized after 288 h of exposition to controlled humidity. After mass stabilization was reached, unmodified fibers showed remarkable higher moisture adsorption (25.0±0.5%) in relation to modified fibers. Only cellulose fibers modified by $T_{12}C_{4.2}$, $T_{12}C_{8.4}$, $T_{24}C_{1.9}$ and $T_{24}C_{4.2}$ conditions have reached the mass stabilization after 384 h, while $T_{18}C_{4.2}$ and $T_{18}C_{8.4}$ samples achieved the stability of the moisture adsorption after 480 h. Deposition of SiO_2 nanoparticles have decreased the hydrophilic character of the cellulose fibers. Nevertheless, the results did not show a clear relation between time reaction and moisture adsorption of the fibers (Figure 2). This result may be partially attributed to heterogeneity in diameter and distribution of SiO_2 particles in the different modification conditions, which directly influences hydrophilic capacity of the fibers. Fibers modified using 18 h of reaction presented the lower moisture adsorption (between 12.3% and 13.0%). Increasing the TEOS content seems to decrease moisture adsorption, as expected due to the decrease of the free hydroxyls available at the fiber surface when SiO_2 particles are present.

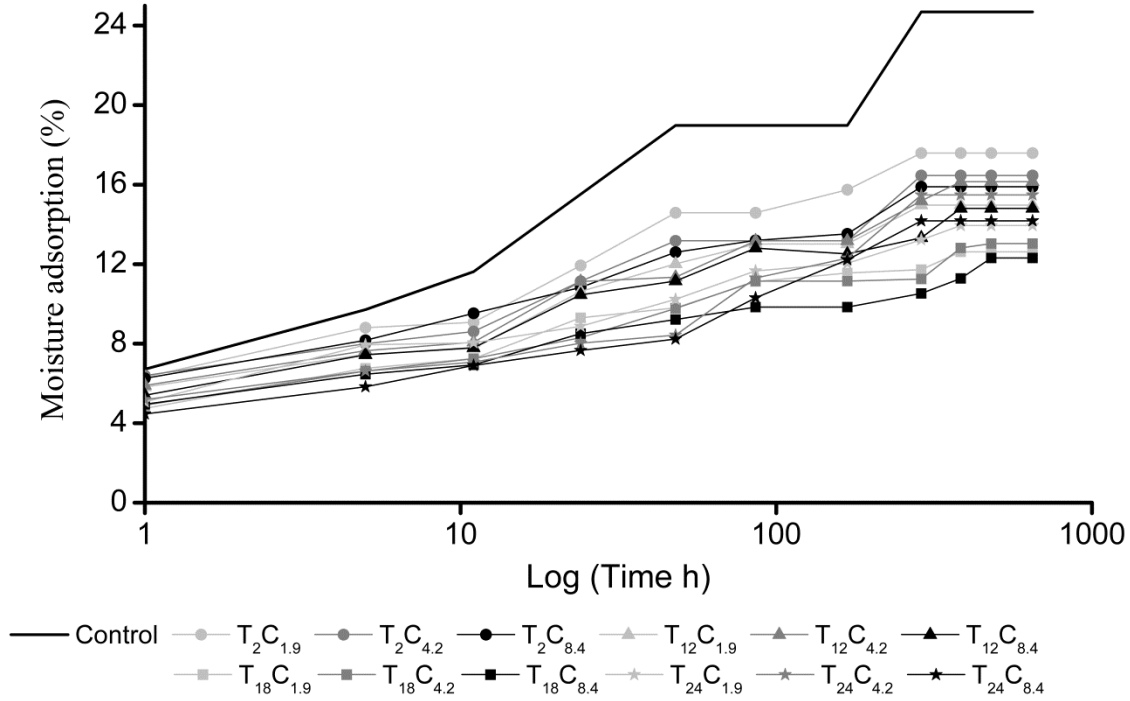

Figure 2. Moisture adsorption of unmodified and modified fibers.

Apart from improving moisture adsorption, it is expected that deposition of SiO_2 particles on cellulose fiber surface improve the dispersion of the cellulose fibers when applied as composite reinforcement in apolar matrices (Felix and Gatenholm, 1991). This is because the reduction of the free hydroxyl groups available at the fiber surface, decreases the strong interactions between fibers (Hubbe et al., 2007). Other benefits from using these modified fibers include the improvements in dimensional stability of the fibers, and the increase in the fiber surface area. As a result, increases in the interaction between composite phases may lead to the improvement of the mechanical strength (Mathew et al., 2005). In the fiber-cement composites, the higher the fibrillar surface of the fibers, the higher the capacity of the fibers to bond with the cement matrix (Coutts, 2005). These results can be interesting for ongoing research in the direction of fiber modification strategies for application of the cellulose fibers as durable reinforcement in different advanced composites.

CONCLUSIONS

Surface modification of cellulose fibers by SiO_2 nanoparticle deposition was successfully achieved for all conditions proposed in this study. Modification time and TEOS precursor content directly influence the amount of Si deposited on the fiber surface, the nanoparticle diameter distribution and resistance to moisture adsorption. There is a tendency of increase in the nanoparticle size and the amount of Si deposited with increasing reaction time. It was observed a reduction of up to 50% in the moisture adsorption capacity of the modified cellulose fibers. The present study contributes to the widespread use of the cellulose fibers and with information for understanding the major mechanisms that influence the mechanical and physical performance of cellulose based materials. The fiber modification used here led to distinct morphological and structural characteristics of the cellulose fiber, which can be used to engineer fiber-cement composites for multipurpose applications.

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