EXTRUDED FIBER-CEMENT COMPOSITES REINFORCED WITH SURFACE-MODIFIED CELLULOSE FIBERS

Rafael Farinassi Mendes[1], Danillo Wisky Silva[1], Ronaldo Soares Teixeira[2], Holmer Savastano Junior[2], Lourival Marin Mendes[1], Gustavo Henrique Denzin Tonoli[1*]

[1] Department of Forest Science, Universidade Federal de Lavras, C.P. 3037, 37200-000 Lavras, MG, Brazil.
*CORRESPONDING AUTHOR: gustavotonoli@yahoo.com.br
[2] Department of Biosystems Engineering, Faculdade de Zootecnia e Engenharia de Alimentos, Universidade de São Paulo (USP), Avenida Duque de Caxias Norte, 225, Pirassununga, SP, 13635-900, Brazil.

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ABSTRACT

The objective was to evaluate the physical-mechanical performance of extruded fiber-cement composites produced with surface-modified cellulose fibers. The silanes used for surface modification of the cellulose fibers were methyltrimethoxysilane (MTMS) and isobutyltrimethoxysilane (IBTMS). Surface modification is an attempt to reduce water absorption of the fibers, and it was confirmed by MEV/EDS measurements of the Si content on the fibers. Moisture absorption was reduced in the modified fibers. The cement composites were fabricated with water/cement ratio of 0.3. The treatment of pulps with silanes positively affected MOR and MOE values of the fiber-cement under bending. MTMS-modified fibers led to significant reduction of water absorption of the composites, in relation to those reinforced with unmodified fibers. The modification of the fibers resulted in distinct surface characteristics for water absorption at the cellulose pulp fibers, which led to important changes in the physical and mechanical properties of the fiber-cement performance.

INTRODUCTION

The renewable cellulose fibers are widely available from wood or fibrous plants in most developing countries. They have several interesting advantages, particularly low density and availability everywhere at modest costs and in a variety of morphologies (Stenstad et al., 2008; Kulpinski et al., 2012). Cellulose fibers have a potential as material for matrix reinforcement in polymer or fiber-cement composites (FCCs) (Peijs and Baillie, 2003; Savastano and Warden, 2005; Belgacem and Gandini, 2008; Savastano et al., 2010).

The main drawback associated with cellulose fibers in cement application is their durability in the cementitious matrix and also the compatibility between both phases (Agopyan et al., 2005). The high alkalinity of water in the pore of the cementitious matrix weakens the cellulose fibers, induces their mineralization (Bentur and Akers, 1989; Toledo Filho et al., 2000) and, consequently, yields to the decay of the composite tenacity in the long term. Moreover, the severe weathering conditions to which the composite is exposed induce water uptake and release of the composite, which results in continuous volume changes of the porous cement matrix and the hydrophilic cellulose fibers cell wall. It has been observed, as a consequence of these cycles of water uptake and release, a loss of adhesion at the fibre to cement interface, resulting on the disjointing of reinforcing elements and decay of composite mechanical properties (John et al., 1998).

Surface treatment of cellulose fibers reduces their hydrophilic character and improves their adhesion with the matrix (Karade et al., 2005; Belgacem and Gandini, 2008; Hoikkanema et al., 2011; Raquez et al., 2012). The reactive hydroxyl groups of the fiber's surface are modified by esterification, etherification, and urethane formation, among many others. As a result, the water absorption (WA) of the composites is reduced and their mechanical properties are improved.

The use of silane coupling agents is a very well-known practice in glass–fibre based composites and silica-filled polymeric matrices (Plueddemann, 1991). These chemicals were applied to cellulose fibre-reinforced polymeric composites (Abdelmouleh et al., 2007) and carbon fibre-reinforced cement paste (Xu and Chung, 2001), as well as in wood fibre–cement materials (Blankenhorn et al., 2000; Pehanich, Blankenhorn and Silsbee, 2004). Although the innovative character of these reports, there is still a relevant lack of information, as the most appropriate silane and the best grafting conditions for a good adhesion between fibre and cement matrix, besides significant reduction of the fibre's hydrophilic character. Horeover, the stability of the fibre's modification can be questioned under the composites processing conditions, namely, during the de-watering and pressing stages. Furthermore and to the best of our knowledge, the effect of the silane modification on the water absorption and porosity of extruded fibre–cement composites reinforced with surface modified eucalyptus pulp has never been previously investigated. Extrusion permits the use of low water:cement ratios (between 0.20 and 0.40), which can further assist in the preservation of the fibers from mineralization. The objective of the present work is to evaluate the impact of surface modification of eucalyptus cellulose fibers with different silanes on the physical and mechanical performance of extruded fiber cement composites.

2. MATERIAL AND METHODS

2.1 Cellulose surface modification

Conventional bleached eucalyptus kraft pulp was used as starting material. The choice of the bleached pulp is due to the fact that these fibers are free of surface contaminants (such as lignin and extractives) that could disturbef the binding of the silanes on the pulp fiber surface. Those bleached fibers are readily available in the Brazilian market and were provided by Fibria company. The individual pulp fibers used have a mean length of around 0.64 mm and average width of around 17.9 μm. Their constitution is of around 84% of cellulose (alpha, beta and gamma cellulose of around 92.2%, 6.8% and 1.0%, respectively), around 15% of hemicellulose and 1% ash content.

The silanes used for the surface modification of the cellulose fibers were methyltrimethoxysilane (MTMS) and isobutyltrimethoxysilane (IBTMS). The experimental design for the chemical modification of the fibers is presented in Table 1. The silanes were prehydrolysed for 2 h under stirring in 50/50 v/v ethanol-distilled water. Then, cellulose pulp was added to the prehydrolysed silane and the resulting suspension was maintained for 4 h under stirring at 1400 rpm. At the end of reaction, the pulp was filtered and the fibers were immediately subjected to heat treatment at 110°C for 12 h, to promote the chemical coupling of reagents, according to the methodology proposed by Abdelmouleh et al. (2004).

Table 1 – Silane concentrations used in the cellulose fibers

Treatment	Silane type	Concentration (% by mass)
1	-	-
2	IBTMS	10
3		25
4		50
5	MTMS	10
6		25
7		50

2.2. Characterization of the chemical modification

For evaluation of the chemical modification, the dried fibers were individualized in water with mechanical agitation, and subsequently filtered to form a cellulose hand sheet, that was pressed under 3.5 MPa for formation of a flat paper with 250 g/m². The fibers were evaluated by SEM micrographs in a Zeiss DSM 940A 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 mm² and 132 eV resolution was used to detection and semi-quantitative analysis of the Si atoms at the fiber surface. Average percentage of Si (% by mass) was obtained after five scans per sample in a 1 mm^2 area. The fiber sheet samples were bonded over a carbon tape on the metallic stubs and carbon coated (for EDS measurements) before testing.

The moisture adsorption test was performed according to ASTM E-104-85 (1996) standard. For each treatment, three replicates were evaluated, with dimensions of 2.0 x 1.0 x 0.1 cm (length, width and thickness, respectively). The samples were oven dried at 70°C for 24 h, and subsequently disposed in a desiccator hermetically sealed at a temperature of 20±2°C and 99% of relative humidity. A saturated solution of potassium sulphate was used to maintain the relative humidity constant. The moisture adsorbed by the samples over time was determined by successive weighting them on a scale with precision of 0.0001 g. This evaluation was carried out for 192 h. The moisture adsorbed (MA) was calculated according to eq. (1):

$$MA\ (\%) = [(M1 - M0) / (M0)] \times 100 \quad (1)$$

Where, MA = Moisture adsorbed; M1 = wet mass (mass of the sample after x hours of exposure to 99% humidity); and M0 = initial mass (before exposure to moisture).

2.3. Composite production and characterization

Cement based composites were reinforced with unmodified and modified pulp fibers. Fiber-cement formulation was based on previous studies (TEIXEIRA et al., 2012; TONOLI et al., 2010). Composites were produced in laboratory small scale by extrusion procedure. The constituents were (percentage by dry mass): 5% of bleached eucalyptus kraft pulp, 60% of ordinary Portland cement (OPC) CPV-ARI (ASTM C150, 2009), 33% of ground carbonate, 1% HPMC (Hidroxipropelmetilcelulose) and 1% ADVA (polyeter

carboxylic aditive). The water:cement ratio used was of around 0.40. The composites were produced with dimensions of 200 mm x 50 mm x 15 mm (length, width and thickness, respectively). After the completion of the curing stage, the specimens were tested 28 days after production. The specimens were soaked in water for 24 h prior to mechanical (Modulus of rupture (MOR) and modulus of elasticity (MOE) at static bending) and physical tests (water absorption (WA) and bulk density (BD)).

2.4 Soak and dry accelerated ageing cycles

Composites were successively immersed into water at 20°C ± 5°C for 170 min, after resting for 10 min, they were heated to a temperature of 70°C ± 5°C for 170 min in a ventilated oven. An interval of 10 min (at room temperature) is usual prior to beginning the next cycle, as recommended by EN 494 (1994) standard. Each soak and dry set represents one cycle, which was repeated 200 times, i.e., 200 ageing cycles. This method simulates natural ageing in severe conditions, although additional studies are needed to simulate the most relevant accelerated conditions corresponding to natural weathering, in order to predict more precisely the long-term behavior of the composites produced. Physical and mechanical performance of the composites, before and after the soak and dry accelerated ageing cycles, were evaluated for comparative analysis of the composites degradation.

3. RESULTS AND DISCUSSION

3.1.Characterization of the fiber modification

Figure 1 shows semi-quantitative data (from EDS measurements) of the Si content (by mass) grafted on the cellulose fibers under the different grafting conditions. The Si content of all the modified fibers was far higher in relation to control (unmodified) sample. Remarkable increase in the average Si content was observed when the concentration of the silanes was increased. In general, the higher concentrations (50% by fiber mass) of MTMS and IBTMS were the most efficient conditions for grafting of the cellulose fiber surface. For MTMS it was not observed statistical differences between the silane concentrations (25% and 50%).

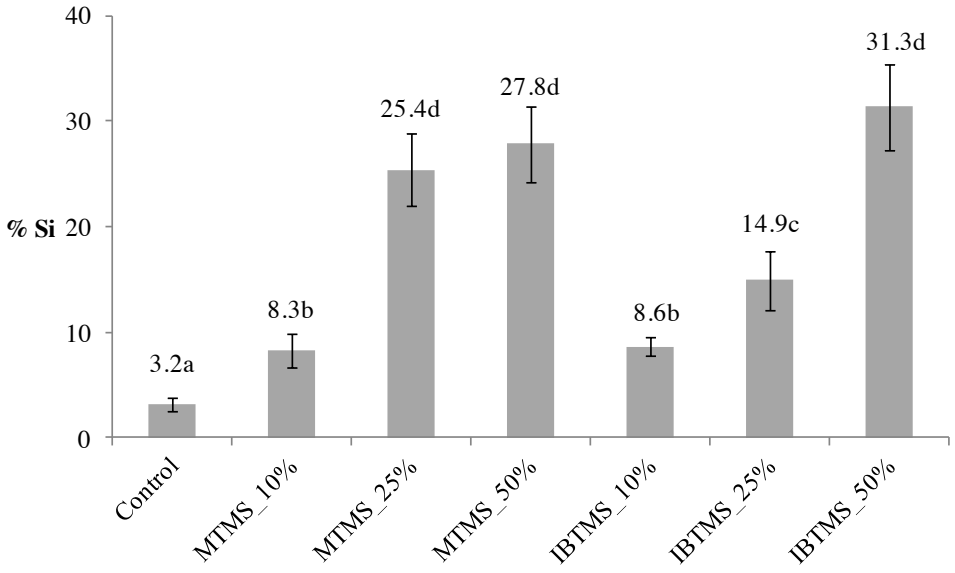

Figure 1 – Average values and standard deviation of the Si content (by mass) grafted on the fiber surface, determined by EDS measurements. Different letters represent statistical differences between the samples (Scott-Knott, 5% significance).

The initial average moisture adsorption (6 h of evaluation) and the final average moisture absorption (192 h of evaluation) for cellulose pulps chemically modified with different silanes in different concentrations can be observed in Figure 2. The high moisture absorption by the cellulose fibers can be associated to the decrease in mechanical properties, dimensional changes and decay on the durability of the composites (ASHORI et al., 2012).

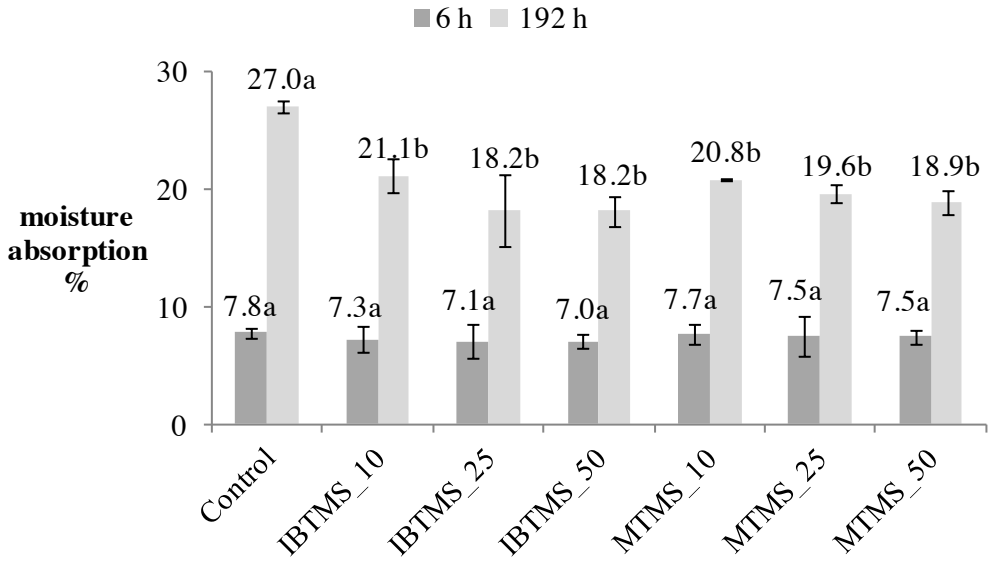

Figure 2 – Initial (after 6 h) and final (after 192 h) moisture adsorption of cellulose pulps chemically modified. Different letters represent statistical differences between the samples (Scott-Knott, 5% significance).

There was a slight decrease in the values of moisture adsorption (21.6 at 32.6 of reduction values) in the grafted cellulose pulps when compared to ungrafted cellulose pulp ($\alpha < 0.05$) after 192 h. There was no statistical difference between the moisture adsorption of the different grafting conditions. The concentration of 25% of silanes seems to be enough for proper modification of the pulp fibers, and then it was chosen for grafting the fibers used in the production of the composites.

3.2 Effect of fiber modification on the mechanical and physical performance of the fiber-reinforced composites

Table 2 shows the effect of pulp modification after 28 days of air curing and accelerated ageing cycles in the mechanical and physical properties of the composites. It is observed that all treatments with modified cellulose pulps have significantly increased the density of the composites after 28 days of curing. This fact can be explained by the formation of chemical bonds between the treated cellulose fibers and cement matrix, thus ensuring better fiber-matrix interaction and consequently higher density, which reflect on significant higher values of MOE and MOR. Pehanich et al. (2004), when considering the modification of cellulose with alkilalkoxisilano, also obtained significant improvement of the MOE and MOR values during bending tests. Those authors similarly justified the increase by the better linking of the fibers with the cement matrix.

Table 2 - Average and standard deviation values for modulus of rupture (MOR), modulus of elasticity (MOE), water absorption (WA) and bulk density (BD) of the fiber–cement composites.

Fiber condition	Composites condition	MOR (MPa)	MOE (MPa)	WA (%)	BD (g/cm³)
ungrafted		6.4 (0.2)	2994 (175)	23.0 (1.1)	1.75 (0.03)
MTMS	28 days	8.0 (0.3)	4718 (335)	21.3 (0.1)	1.82 (0.03)
IBTMS		7.6 (0.4)	4419 (558)	24.7 (2.0)	1.81 (0.05)
ungrafted		6.2 (0.6)	3453 (424)	15.5 (1.5)	2.00 (0.04)
MTMS	200 cycles	8.6 (0.9)	5360 (861)	11.0 (2.5)	2.07 (0.03)
IBTMS		8.5 (1.3)	5428 (860)	15.9 (3.4)	1.92 (0.04)

MOR values decreased after accelerated aging for fiber-cement produced with ungrafted cellulose pulp. For composites produced with cellulose pulp grafted with silanes the MOR values increased after ageing, attending Brazilian standard (NBR 15498, 2007) for flat fiber cement boards. The use of grafted cellulose fibers led to improved mechanical performance even after accelerated ageing. MOE values increased for all treatments. According to Mohr, Nanko and Kurtis (2005) and Tonoli et al. (2009a) these results are due to the re-precipitation of hydration products around the fibers, which improves the transition zone around the fibers by decreasing the porosity of the composite. Consequently, BD values also increased with accelerated ageing (Table 2).

4. CONCLUSIONS

Results obtained with MEV/EDS and moisture absorption indicated differences between the cellulose pulps ungrafted and cellulose pulps grafted with silanes. These observations point out that modifying surface of the fibers with silanes is a promising approach to fiber hydrophobization. The concentration of 25% of silanes seems to be enough for proper modification of the pulp fibers. Fiber grafting with silanes positively affected the mechanical properties (MOR and MOE values) even after accelerated aging. MTMS-grafted fibers significantly reduced the water absorption of the composites in relation to ungrafted fibers. These results contribute in the direction of efficient fiber modification strategies aiming to improve adhesion and long term performance of the fiber-cement composites.

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5. REFERENCES

Abdelmouleh, M. et al. 2004. "Modification of cellulosic fibres with functionalised silanes: development of surface properties". International Journal of Adhesion and Adhesives. 24(1) 43-54.

Abdelmouleh, M., Boufi, S., Belgacem, M.N., Dufresne, A. 2007. "Short natural-fibre reinforced polyethylene and natural rubber composites: effect of silane coupling agents and fibres loading". Compos Sci Technol 67(7–8)1627–39.

Agopyan, V., Savastano, Jr H., John, V.M., Cincotto, M.A. 2005. "Developments on vegetable fibre–cement based materials in São Paulo, Brazil: an overview". Cem Concr Compos. 27 (1) 527–36.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. ASTM C 150-09. 2009. Standard Specification for Portland Cement. West Conshohocken, PA, USA.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. ASTM. E-104-85. 1996. Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions. Filadélfia.

Ashori, A. et al. 2012. "Bacterial cellulose/silica nanocomposites: Preparation and characterization". Carbohydrate Polymers. 90(1) 413– 418.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 15498. 2007. Asbestos cement flat board - Requirements and test methods. Rio de Janeiro, Brasil, 26p. (In Portuguese)

Belgacem, M.N., Gandini, A. 2008. "Monomers, Polymers and Composites from Renewable Resources". Elsevier, Amsterdam.

Bentur, A., Akers, S.A.S. 1989. "The microstructure and ageing of cellulose fibre reinforced cement composites cured in a normal environment". Int J Cem Compos Lightweight Concr 11(2) 99–109.

Blankenhorn, P.R., Blankenhorn, B.D., Silsbee, M.R., Dicola, M. 2001. "Effects of fiber surface treatments on mechanical properties of wood fiber–cement composites". Cem Concr Res 31 1049–55.

European Standard, EN 494. 1994. Fibre–cement profiled sheets and fittings for roofing – products specification and test methods.

Hoikkanema, M., Honkanenb, M., Vippolab, M., Lepistob, T., Vuorinena, J. 2011. "Effect of silane treatment parameters on the silane layer formation and bonding to thermoplastic urethane". Progr. Org. Coating 72 716 – 723.

John, V.M., Agopyan, V., Prado, T.A. 1998. "Durability of cement composites and vegetable fibres for roofing". In: Proceedings of 3rd Ibero-American symposium on roofing for housing. São Paulo: Cyted/USP 51–9 [in Portuguese].

Karade, S.R., Irle, M., Maher, K. 2005. "Assessment of wood-cement compatibility: a new approach". Holzforschung 57(1) 672 – 680.

Kulpinski, P., Erdman, A., Namyslak, M., Fidelus, J.D. 2012. "Cellulose fibers modified by Eu 3 + -doped yttria-stabilized zirconia nanoparticles". Cellulose 19 (1) 1259 – 1269.

Mohr, B. J.; Nanko, H.; Kurtis, K. E. 2005. "Durability of kraft pulp fiber-cement composites to wet/dry cycling". Cement and Concrete Composites 27(4) 435-448.

Pehanich, J.L., Blankenhorn, P.R., Silsbee, M.R. 2004. "Wood fiber surface treatment level effects on selected mechanical properties of wood fiber–cement composites". Cem Concr Res 34 (1) 59–65.

Peijs, T., Baillie, C. 2003. "Eco-composites (A special issue of 14 publications devoted to cellulose-based composite materials)". Compos. Sci. Technol. 63(9) 1223-1336

Plueddemann, E.P. 1991. "Silane coupling agents". 2nd ed. New York: Plenum Press; 272p.

Raquez, J.M., Murena, Y., Goffin, A.L., Habibi, Y., Ruelle, B., Debuyl, F., Dubois Aibi, P. 2012. "Surface-modification of cellulose nanowhiskers and their use as nanoreinforcers into polylactide: a sustainably-integrated approach". Compos. Sci. Technol. 72:544 – 549.

Savastano Jr., H., Warden, P.G. 2005. "Special theme issue: natural fibre reinforced cement composites". Cem. Concr. Compos 27 517 – 624.

Savastano Jr., H., John, V.M., Agopyan, V., Moslemi, A. 2010. "Special issue on inorganic-bonded fiber composites". Constr. Build. Mater. 24 129 – 220.

Stenstad, P., Andresen, M., Tanem, B.S., Stenius, P. 2008. "Chemical surface modifications of microfibrillated cellulose". Cellulose 15 35 – 45.

Teixeira, R.S. et al. 2012. "Extruded cement based composites reinforced with sugar cane bagasse fibres". Key Engineering materials 517 450-457.

Tolêdo Filho, R.D., Scrivener, K., England, G.L., Ghavami, K. 2000. "Durability of alkalisensitive sisal and coconut fibres in cement mortar composites". Cem Concr Compos 22(2) 127–43.

Tonoli, G. H. D.; Fuente, E.; Monte, C.; Savastano Junior, H.; Rocco Lahr, F.A.; Blanco, A. 2009. "Effect of fibre morphology on flocculation of fibre–cement suspensions." Cement and Concrete Research 39(11) 1017-1022.

Tonoli, G. H. D. et al. 2010. "Eucalyptus pulp fibres as alternative reinforcement to engineered cement based composites." Industrial Crops and Products 31(2) 225-232.

Xu, Y., Chung, D.D.L. 2001. "Silane-treated carbon fiber for reinforcing cement." Carbon 39 1995–2001.