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Effect of hornification on the structure, tensile behavior and fiber matrix bond of sisal, jute and curauá fiber cement based composite systems

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HIGHLIGHTS

- Natural fiber tensile strength can be increased with the application of the hornification treatment.
- New bonds between polymer chains in the microfibrills can be created with hornification.
- Cellulose crystallinity can be altered with the used treatment.
- Significant improvements in the fiber-matrix interface were verified through hornification.

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ABSTRACT

Several fiber treatments are used to mitigate the high water absorption of vegetable fibers. Wetting and drying cycles are usually performed in the industry of paper and cellulose to reduce the volume variation of these fibers. This procedure stiffens the polymeric structure of the fiber-cells (this process is known as hornification) resulting in a higher dimensional stability. The aim of this study is to determine the effect of the hornification on the chemical and mechanical behavior of natural fibers and how these properties influence the fiber matrix bond. For this purpose, 5 and 10 cycles of wet and drying were applied to curauá, jute and sisal fibers. Fiber pull-out tests were performed in the embedment length of 25 mm. Direct tensile tests were performed in natural and hornified fibers. Furthermore, X-ray diffraction, thermogravimetry analysis, infra red spectroscopy and nuclear magnetic resonance were used to investigate the influence of the hornification on the chemical properties of the studied fibers. Modifications on the fiber morphology were observed with a scanning electron microscope. The results indicate changes on the tensile strength and strain capacity of the studied fibers, showing that morphology, physical aspects and chemical composition play an important role on the efficiency rate of hornification. Significant improvement in the fiber-matrix interface was observed through the pullout tests. It was concluded that 5 cycles promotes a better performance to curauá and sisal fibers. Only the sisal fibers show improvement on its bond mechanisms after 10 cycles.

1. Introduction

Vegetable fiber reinforced composites have the potentiality to become the ultimate green material option, minimizing the use of natural resources and overall lifetime impact. Due to its wide availability, especially in tropical countries, these fibers have a low cost and present the great advantage of being renewable. Regarding the drawbacks in the use of those fibers, treatments have been studied to reduce the impact of a low chemical bond and the high water absorption capacity which causes a volumetric instability. This volumetric instability results in a partial loss of the fiber-matrix physical contact damaging the interfacial transition zone.

Several fiber treatments can be used to reduce the natural fibers volumetric instability and increase their affinity with a cementitious matrix [1,2]. These procedures can clean the fiber surface, modify its chemistry, lower the moisture uptake and increase the surface roughness [3]. As natural fibers bear hydroxyl groups from cellulose and lignin, they are subject to chemical modification. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules thereby reducing the activity towards the

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matrix. Chemical modifications may activate these groups and can introduce new moieties that can effectively lead to a chemical interlock with the matrix [4,5]. Mercerization, isocyanate treatment, acrylation, permanganate treatment, acetylation, methane cold plasma, silane treatment and peroxide treatment with various coupling agents and other pretreatments of natural fibers have achieved various levels of success for improving fiber strength, fiber stiffness and fiber-matrix bond [2,6–8]. Furthermore, thermal treatments can also be used to improve the natural fiber properties [9,10]. Usually a combination of chemical and thermal treatments are applied. Acid and alkaline treatments were proposed by Abou-Yousef et al. [9] as a solution for sugar cane delignification. At 200 °C, the loss of material due to pyrolysis is still low, and only the extractives and hydrogen bonds are destroyed [11]. Depending on the type of lignocellulosic fiber, partial lignin may be removed in this process [12]. The application of the mentioned treatments have shown to be effective in promoting changes in the natural fiber morphologies as well as in their physical and mechanical behavior [1]. A particular procedure to reduce the water absorption capacity of natural fibers and to improve the fiber-matrix bond have been pursued by applying cycles of wetting and drying in the fibers [1,2,13]. These treatments promoted a reduction in volumetric changes of pulps and fibers of natural origin as well as alterations in their mechanical properties. This is a result of repeated wetting and drying cycles which increase the degree of crosslink within the fiber microstructure. Fibers treated by methane cold plasma during 10 min presented a higher hydrophobicity. The treatment promoted a better adhesion with the cement matrix which was confirmed by pullout tests [8]. The use of carboxylated styrene butadiene polymer latex not only promotes a fiber surface that is hydrophobic but the polymer latex acts as a bridge between fiber and the cementitious matrices, strengthening the interfacial bonding between them [2,4]. The fiber hornification treatment have been successfully used by Claramunt and co-workers in vegetable fiber reinforced cement composites [14]. The previous treatment of the fibers improved the durability and also the mechanical behavior of the studied cement based composites. However, there still exists a lack of information on how the use of such treatment modifies the chemical properties and morphology of the natural fibers affecting the fiber-matrix bond with a cement based matrix. The objective of the present research is to investigate the effect of cycles of wet and drying on the fiber properties (chemical and mechanical) and fiber-matrix interface behavior of natural sisal, curauá and jute fibers. Tensile tests were carried out to study the effect of the treatments on the fiber. After the treatments, the fibers were analyzed through SEM, thermogravimetry and X-ray diffraction. Pullout tests were carried out to investigate the potential benefits caused by the treatments in the interface bond.

2. Experimental program

2.1. Materials and processing

The sisal fibers used in the present study were obtained from the sisal plant (*Agave sisalana*) cultivated in farms located in the Bahia state, Brazil. They were extracted from the sisal plant leaves in the form of long fiber bundles. Sisal fibers are extracted from the leaf by a process called decorticaion. In this process, the leaves are crushed by a rotating wheel with blunt knives, where only the fibers prevail [15]. Decorticated fibers were dried under the sun light. The curauá fibers were provided by the company Pematec, located in the city of Santarém, in the state of Pará, Brazil. The curauá fibers are produced in the Amazon region, and extracted from the leaf of the plant *Ananas erectifolius* by a process similar to the process used for sisal fiber. The jute fiber came from the Amazon region. It is extracted from the stem of the plant *Corchorus capsularis* by a combination of processes which comprises the following steps: cutting, retting, shredding, drying, packing and classification [15].

Regarding to the natural fiber microstructure it is formed by numerous individual fibers (fiber-cells) (see Fig. 1). The individual fiber-cells are linked together by means of the middle lamella. More information on the studied fibers microstructure can be found in the authors previous works [1,16]. Even though all natural fibers present a similar morphology the cell wall size, thickness, porosity and cross-section area may vary. This variation between fibers can result in a different mechanical behavior. According to Fidelis et al. [15] curauá, jute and sisal fibers can present an average tensile strength of 540, 250 and 480 MPa, respectively. These natural fibers can be classified as high performance fibers. Not only the morphology but also the chemical composition rules the fiber mechanical behavior. These fibers present a different amount of cellulose, each one presenting a different crystallinity degree. Another important parameter correlated to the tensile strength is the microfibrillar angle. According to Satyanarayana and Mukherjee [17,18], curauá, jute and sisal has a microfibrillar angle of 18.8°, 17.1° and 20°, respectively. Fidelis et al. [15] correlate the mechanical strength of natural fibers not only to cellulose content, but also due to a high microfibrillar angle. Coir fibers, with a microfibrillar angle of 8°, present a tensile strength of 177 MPa and modulus of 3.4 GPa while Jute fibers have a tensile strength of 353 MPa and a modulus of elasticity of 26 GPa. It is still not well understood how the combination of all the aforementioned parameters influence the mechanical performance of the natural fibers. The chemical composition of the used natural fibers are shown in Table 1. More information on the natural fibers microstructure and mechanical properties can be found in the authors previous work [15,19,20].

The used matrix presented a mix design of 1:0.5:0.4 (binder: sand: water/binder ratio) by weight following the author's previous works [21]. The binder was composed by 30% of Portland cement CP II – F32 defined by the Brazilian standard [22] as composed with filler (in mass: 85% < clinker < 91%; 3% < gypsum < 5%; 6% < limestone filler < 10%) with 32 MPa of compressive strength at 28 days. Following the recommendations of previous studies, in order to increase the durability of the composites, the Portland cement was replaced by 30% of metakaolin (MK) and 40% of fly ash. This ratio of metakaolin and fly ash aims to guarantee the durability of the fiber once a matrix free of calcium hydroxide is obtained, as shown in the previous research [16]. The fly ash also ensures greater workability to the matrix that, within the context of high-performance composites, is a desirable property as it ensures a better homogenization of the vegetable fibers [1].

The sand was processed to obtain a maximum diameter of 840 μm. The used superplasticizer was the Glenium 51 (type PA) with solids content of 31%. A viscosity modifier Rheomac UW 410, (manufactured by BASF), at a dosage of 0.8 kg/m^3 was also used in order to avoid segregation and bleeding during molding. The matrix used in this study showed a flow table spread value of 450 mm according to ASTM C1437 [23] and compressive strength at 28 days of 31 MPa, according to ASTM C 39 [24].

The mixtures were produced in a room with controlled temperature (21 ± 1 °C) using a mixer with capacity of 5 L. The mixing procedure is described as follow. All dry components were homogenized in the mixer. The water and superplasticizer were added and mixed for 2 min at a speed of 125 RPM. After that, the process was stopped during 30 s to remove the material retained in the mixer. Then, the mixing procedure continued for 2 min at 220 RPM and, finally for a further 5 min at 450 RPM.

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