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Evaluation of cellulosic pulps treated by hornification as reinforcement of cementitious composites

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HIGHLIGHTS

- Hornification treatment does not deteriorate the fiber quality.
- Hornificated pulps show good behavior as reinforcement for composites at early ages.
- Hornification process presents potential to be used as a treatment for cellulosic pulps.

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ABSTRACT

This study evaluated the effect of the hornification process on cellulosic fibers of bleached pine and unbleached eucalyptus with in order to improve its durability and volume stability to be used as reinforcement in cementitious matrices. The study indicated that the treatment did not deteriorate the properties of viscosity and index of crystallinity and decreased the capacity of water retention. Composites reinforced with hornificated and untreated pulps with thermal curing or accelerated aging were produced and evaluated to assess their physical and mechanical behavior. The use of hornificated fibers as reinforcement generated improvements in the modulus of rupture and specific energy of the composites.

1. Introduction

It is well known that construction industry is responsible for solid waste production, large consumption of non-renewable resources for several materials production and release of green house effect gases to the atmosphere [1,2], being responsible for the generation of approximately 30% of CO_2 world emissions [2]. Thus, a necessity of minimizing environmental and health problems arose which stimulated different research studies to develop new materials from alternative raw material sources, remarking vegetable fibers as reinforcement materials in cementitious matrices [3,4]. The use of this type of fiber generated great interest by offering a wide number of advantages, which stands its low cost when compared to synthetic fibers, high availability, low density, renewable resource nature and solid waste reuse [3]. In addition, composites made from these fibers have shown good performance of thermal properties [5].

The use of long fibers (e.g. Pinus) as reinforcement is common in fiber cement products on the current market [6]. These fibers generally perform better than short fibers (e.g. Eucalyptus) [7,8], as they have higher anchorage length. Moreover, they are thicker fibers with thick cell walls and therefore, they are stronger compared to fibers with thin cell walls [8]. Regarding short fibers, its use is economically more favorable [6], their lower fiber length allows a higher concentration of fibers per gram, improving their dispersion and distribution within the matrix [9], favoring the performance of the material.

The reinforced composites have a different behavior compared to not reinforced composites when its maximum tensile strength is overcome. The latter show an abrupt break with null strain, typical for brittle materials. The main purpose of reinforcing fragile cement matrices from plant fibers is to obtain a better mechanical performance for the composite in practical applications [10]. The

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material must display superior functional characteristics when compared with the conventional material, for example, an increase in flexural strength reaching a ductile behavior, greater energy absorption capacity before failure, cracking control and prevention. It also allows the use of the material in post-cracked conditions [11] and a better fatigue and thermal conductivity resistance [12]. Several studies showed positive results regarding the performance of cementitious matrices reinforced with vegetable fibers [13–15].

However, the use of vegetable fibers as reinforcement in cementitious composites exhibits some drawbacks associated to two factors which are considered crucial: (1) degradation of the fiber constituents (lignin and hemicellulose) and reduction of the degree of polymerization in the alkaline environment of the matrix and (2) physical incompatibility (lack of adherence) between the fibers and the matrix in relation to dimensional variations of the fibers by its hygroscopicity. The decrease in the degree of reinforcement in the composites can be attributed to the decrease in fiber pullout, being this decrease explained by several factors working in conjunction, such as weakening of the fibers caused by the alkaline attack, mineralization of the fibers by migration of cement hydration products to the core of the fibers and generated gaps by fiber dimensional change [16].

Several alternatives to extend the life of the plant fibers can be based either on the fiber processing or on modification of the cementitious matrix [17,18]. The hornification treatment arises as a pre-treatment of the fibers. Hornification is a technical term to describe changes and structural alterations in the cellulosic fibers originated from either dewatering or recycling of the fibrous pulp [19]. During the hornification process, inside the fibers, the fibrils are in contact after drying [20] and the cellulose polysaccharide chains are grouped closely together (firm packaging) with water removal [21], causing the binding of microfibrils as a flat strip [22,23]. This all leads to the irreversible loss of water retention capacity of the fibers [22,24] and the collapse of the vegetable fiber without dramatically altering their strength properties [25,26].

The reduction of the water retention capacity of the cellulosic fibers may have beneficial effects when incorporated as a reinforcement for cement matrices, since these fibers have greater dimensional stability, providing better adhesion between fiber–matrix and reducing the formation of fouling hydroxide calcium on the surface and lumen of the fibers, resulting in a reduction in the degradation of cellulose in the cement matrix [27].

In this study, physical–mechanical performance of cement matrices reinforced with unbleached eucalyptus and bleached pine pulp hornificated by four drying and wetting cycles was analyzed. The physical–mechanical behavior of composites was evaluated after thermal curing and 200 accelerated aging cycles.

2. Materials and methods

2.1. Materials

Unbleached hardwood kraft pulp of eucalyptus (*Eucalyptus grandis* e *Eucalyptus urophylla*) and commercial bleached softwood kraft pulp of pine (*Pinus radiata*) supplied by private companies were used as a reinforcement. Unbleached eucalyptus pulp (UnBE) was taken at the beginning of the bleaching process and disintegrated with 65% relative humidity and bleached pine pulp (BP) was presented in a dry sheet form with 10% relative humidity. As cementitious matrix high early strength Portland cement (CPV-ARI) according to ASTM-C150 Standard [28] and limestone were used. The oxide composition of the components of the matrix is showed in Table 1.

2.2. Pulp treatment

The hornification process of the pulps consisted of four cycles of drying and rewetting, as follows: (1) pulp drying in an oven with air circulation at 60 °C for 7 h; (2) rewetting by immersion in water at room temperature for 15 h; (3) disintegration of wet cellulose pulp in a disintegrator (3.000 revolutions – 10 min) according Ref. [29]; (4) pulp suspension filtering through a Buchner funnel equipped with a wire screen (150 mesh). At the end of the process (after 4 cycles), the fibers were stored in sealed plastic bags until their subsequent use. The hornification methodologies was taken and modified from Claramunt et al. [27].

Table 1
X-ray fluorescence chemical analysis of the cementitious matrix materials in mass percentage.

Oxide composition	Portland cement – CP V-ARI	Limestone
CaO	63.5	51.7
MgO	2.32	3.04
SiO_2	19.1	1.70
Al_2O_3	4.44	0.21
Fe_2O_3	2.68	0.17
Na_2O	0.36	0.01
K_2O	1.10	0.09
SO_3	2.63	–
MnO	<0.10	0.04
P_2O_5	0.21	0.08
TiO_2	0.24	0.03
Loss on ignition (1000°)	3.52	43.1

2.3. Pulp characterization

2.3.1. Water retention value

The water retention values were determined after and before the hornification process according to the standard Tappi UM 256 [30].

2.3.2. X-ray diffractometry

To measure the crystallinity index of the cellulose pulp before and after the treatment, the technique of X-ray diffractometry (XRD) was used. The crystallinity index of cellulose pulps was determined according to the empirical method suggested by Segal, [31]. This method consists in calculating the index of crystallinity for cellulose (Cr.I.), according to the following Eq. (1):

$$\text{Cr.I.}: \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \quad (1)$$

where I_{002} corresponds to the maximum intensity of diffraction (crystalline) of plane (002) and I_{am} refers to the intensity of the background scatter (amorphous). The values I_{002} and I_{am} were obtained directly from diffractograms of studied pulp.

2.3.3. Viscosity measurements

The viscosity measurements were determined after and before the hornification process according to the standard Tappi 230 om-04. [32]

2.4. Composites production

4 sets of samples composed of 16 specimens each were prepared. The purpose of this stage was to evaluate the behavior of composites reinforced with bleached and unbleached hornificated and untreated fibers, according to their mechanical properties and durability of the fibers before and after the accelerated aging test. One set was prepared with untreated pulp and the other one with hornificated pulp. 8 specimens of each series were subjected to accelerated aging treatment. The experimental composition of the specimens was fixed in mass percentages as follows: 68% cement, 27% limestone and 5% pulp.

For the production and characterization of the composites, flat plates of cement with dimensions of 200 × 200 × 5 mm were molded. The production method is based on raw materials mixing with an excess of water that is removed by vacuum drainage and subsequent mechanical pressing (3.5 MPa for 5 min) according to the procedure described by Savastano et al. [33]. Dried pulps were previously dispersed in water by means of a pulp disintegrator at 3000 rpm for 10 min. Other inputs were added and homogenized for another 10 min using a high speed mechanical stirrer (1700 rpm). The formed suspension was transferred to a molding chamber. For each formulation, plates were pressed individually, and sealed in plastic bags in saturated conditions for two days and then submitted to thermal curing (controlled environment of 90% RH and 55 °C) for 5 days. Upon completion of the cure, the plates were cut into four specimens (160 × 40 mm) with water cooled diamond saw. Series consisting of 8 specimens for each formulation were tested in the saturated conditions (immersed in water 24 h before mechanical testing) and another series of 8 specimens were intended to accelerate aging.