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Nanofibrillated cellulose and cellulosic pulp for reinforcement of the extruded cement based materials

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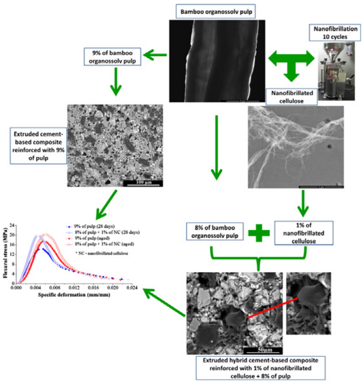
HIGHLIGHTS

- The high specific surface area of NC improves the fiber-matrix bonding.
- The NC improves the stress transfer when the composite is subjected to load.
- At 28 days the hybrid composite presents a higher modulus of rupture.
- In the hybrid composite, the NC acts as nanoreinforcement after accelerated ageing.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of cellulose nanofibers as reinforcement may contribute for improving particle packing and decrease the crack growth rate of composites at nanoscale. Additionally, the high specific surface area of cellulose nanofibers contributes to improve the adhesion between the cement particles. Thus, the aim of this work was the study the performance of hybrid composites reinforced with 8% pulp and 1% nanofibrillated cellulose compared to composites reinforced with only 9% of pulp produced by the extrusion process. The accelerated aging process by means of 200 wet and dry cycles was carried out to assess composite degradation. In the hybrid composites the nanofibrillated cellulose improved the mechanical behavior compared to the composite without nanofiber. This improvement may be associated with greater adherence between the nanofibrils and the cement matrix. After accelerated ageing, the composites with and without nanofibers showed no reduction in mechanical performance, which is attributed to the lower alkalinity provided by the accelerated carbonation. Therefore, the nanofibrillated cellulose showed to be a promising material for use as nanoreinforcement of the extruded hybrid cement-based composites.

1. Introduction

The cementitious materials are ceramic that originally present a brittle behavior when is subjected to a load i.e. it presents a yield strength similar to tensile strength. A brittle fracture initially takes

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place at the nano and/or interatomic scales without prior plastic deformation during elastic loading, because the ions-covalent bonds of ceramics do not allow the movement of the dislocations at room temperature due the electrostatic restrictions. In fiber-cement it is important to consider the nanomechanical behavior of the calcium silicate hydrate (C–S–H), the binding phase in all cementitious materials, is one of the most complicated and intriguing material systems in materials science and engineering [1,2].

A means of minimize the problem of cracking is through the incorporation of fibers in the cementitious matrix, and consequently the toughness, flexural strength, resistance to cracking and crack propagation are improved. The main advantage of the use of fibers as reinforcement of the cementitious materials is in it post-cracking behavior [3–6]. In this way, mechanical behavior of fiber-cement composites is also characterized by an interfacial transition zone in the vicinity of the reinforcing inclusion, in which the microstructure of the matrix is considerably different from that of the bulk matrix, away from the interface.

The incorporation of nanofibers in the cementitious matrix is a partial solution to the challenge of the cracking, due the nanofibers acting as stress transfer bridges in the nano-cracking. Many studies have been conducted about the use of the nanofibers and carbon nanotubes [7–9], which act as bridges over the cracks in order to create reinforcement mechanisms and to retard cracking in the nanoscale. Thus, there are improvements in flexural and compressive strength of these materials [10–16].

1.1. Nanofibrillated cellulose

The nanofibers from vegetable origin are an alternative for use as nanoscale reinforcement of cementitious materials, since they have additional advantages, such as, abundance worldwide, renewable, have low density and high mechanical strength and stiffness [17–21].

A method for obtaining vegetable nanofibres is the mechanical nanofibrillation. This method causes irreversible changes in the fibers by isolating cell wall. The nanofibrillation occurs from the use of shear force without the need for chemicals, such as hydrolysis in acid. Mechanical fibrillation increases the potential for bonding by modifying the morphology and reducing the size of the fibers [21–23].

According to Ardanuy et al. [24] the high specific surface area of the nanofibrillated cellulose provides a good fiber-matrix bonding. Furthermore, the increase of hydroxyl groups available on the cellulose enables the formation of the hydrogen bonds between nanofibrillated cellulose and cementitious matrix.

1.2. Inorganic matrices reinforced with nanofibrillated cellulose

Some studies have been reported the use of cellulose nanofibers as reinforcing cementitious materials. Ardunay et al. [24] used 3.3% (by mass) of nanofibrillated cellulose from sisal as reinforcement of mortar. The authors reported an increase of the 26.4% in the flexural strength and 41.5% in the modulus of elasticity in the mortar reinforced with nanofibrillated cellulose in comparison to mortar reinforced with the pulp.

Onuaguluchi et al. [25] produced cement pastes by the incorporating of nanofibrillated cellulose from bleached pine pulp at levels of 0.05%, 0.1%, 0.2% and 0.4%. The results showed that the pastes reinforced with 0.1% of nanofibers presented an increase of 106% in flexural strength and 184% in energy absorption, comparing to pastes without nanofiber.

The results of this work show that the use of fibers at the nanometer scale is effective for increasing the mechanical performance of cementitious materials. Additionally, in hybrid composites, two or more fibers with different characteristics and scales are combined to produce a new material, which derives benefits of each individual fiber and displays a synergistic response [26].

In the hybrid composite, microfibers in the pulp form can contribute to a better packing in the cementitious matrix. Hence, it is possible to use higher fiber contents of around 10% by mass, with a good anchoring of the fiber in the matrix and higher number of filaments for a given volume of reinforcement, resulting in improvements in the flexural strength and toughness [27–29].

The fibers of different dimensions, in hybrid composites, act to provide a dense packing and with a better dimensional stability, and from the use of micro and nanometric fibers, they work as reinforcements in the corresponding scales and according to their dimensions.

Besides, there is the reduction of lignocellulosic fiber durability is caused mainly by the alkaline (pH around 12) environment of the cement matrix. The pore water, with high alkalinity, damages the macromolecular chains by means of hydrolysis of the cellulose, which causes their rupture and a consequent decrease of the degree of polymerization of the cellulose chains [30].

The curing process may positively influence the performance of micro and nanometric reinforcements in the cementitious matrix. The accelerated carbonation curing contributes for the refinement of the porous structure and decreasing alkalinity of the cementitious matrix, and thereby there is a better adhesion interface between the particles of the matrix and fibers and better durability of lignocellulosic fibers [31]. As a result there are better stress distribution with nano-reinforcement, densification of the matrix and improvement of the mechanical performance of composites.

Thus, the aim of this study was to evaluate the hybrid cementitious composite reinforced with nanofibrillated cellulose and pulp using as reference composites reinforced only with pulp in order to investigate the effect of the nano-reinforcement in the physical, mechanical and microstructural performance in the extruded composites.

2. Materials and methodology

2.1. Preparation and characterization of pulp and nanofibrillated cellulose

The pulp was obtained from bamboo by the organosolv pulping method, according to Correia et al. [21,32,33]. The pulp was chemical composed by 1.5% of extractives, 14.4% of lignin, 8.8% of hemicellulose and 76% of cellulose, which were, respectively, determinated according to Tappi Standards [34,35] and Morais et al. [36].

The nanofibrillated cellulose was produced from unbleached bamboo organosolv pulp by the grinding method, using a commercial grinder, Supermasscolloider Mini, model MKCA 6-2, with two grinding stones of aluminum oxide (Al_2O_3), model MKGA 6-80#, produced by Masuko Sangyo Co., Ltd., Japan. The nanofibrillation was produced after 10 nanofibrillation cycles, according to Correia et al. [21].

The average distributions of the length and width of the pulp were analyzed using a Pulptec™ MFA-500 Morphology Fibre and Shive Analyser — MorFiTrac, according to Tonoli et al. [37] and Correia et al. [33]. The structure and the size of the nanofibrillated cellulose were examined from the images obtained via Scanning Transmission Electron Microscopy (STEM) (FEI Magellan 400 L Scanning Electron Microscope), according to Correia et al. [21]. The average width of 150 fibers for each sample was measured from the STEM images using the free software for image analysis called ImageJ. The scale of the software was calibrated using the scale bar on the STEM images.