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MECHANICAL PERFORMANCE OF DUCTILE CEMENT MORTAR COMPOSITES REINFORCED WITH NANOFIBRILLATED CELLULOSE

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Abstract

Most of the published works on the field of natural fibre reinforced cement mortar composites, describe the use of natural fibres with several mm in length (2-10 mm) and diameters ranging between 10-30 μm such as wood pulps, sisal and abaca fibres, cotton linters, etc. It is well-known that the reinforcing capability of these fibres can be increased by reducing their size into the nanometre scale. Although the application of nanofibres in polymer composites is widespread, as far as we know, there is a lack of data related to the use of these fibres as reinforcements in cement mortar matrices.

In this work, the performance of ductile cement mortar composites reinforced with cellulose nanofibres has been evaluated and compared with the one of composites reinforced with conventional sisal pulp. To improve the composite degradation, silica fume was replaced partially the portland cement. In addition, the effect of a decrease of sand particles in the performance of the material has been analyzed.

Results show how the use of nanofibrillated cellulose fibres combined with fine sand leads to composites with enhanced both flexural modulus and flexural strength. Nevertheless, the higher values of fracture energy were obtained for the composites prepared with conventional pulps.

1. INTRODUCTION

The combinations of interesting mechanical and physical properties of natural fibres together with their environmental benefits and low costs, have been the main drivers for their use as alternatives for harmful asbestos in cement mortar composites. Due to their low cost vegetable fibre reinforced cement mortar composites (VFRCMC) constitute a very interesting option for the building industry, mainly in less developed countries or countries that need low cost constructions [1]. However, the industrial production of VFRCMC is currently limited by the lack of durability of these materials [2-4]. One possibility for improving the durability of the VFRCMC is to modify the composition of the matrix in order to reduce or remove the

alkaline compounds. Tolêdo Filho et al. used puzzolanic additions to precipitate the calcium hydroxide of the matrix as calcium silicate hydrate, or treatments with a higher concentration of CO_2 to precipitate the calcium hydroxide as calcium carbonate [5, 6]. The use of silica fume in amounts around 30% or greater can improve significantly the durability of the VFRCMC [6, 7]. On the other hand, the optimum cement and sand particle size will facilitate the hydration and the interaction of the mixing compounds. These matrix modifications could lead to an improvement of the intrinsic resistance and rheological behavior of the cementitious past [8].

The fibres typically used in VFRCMC are a few mm in lengths. Micro-sized fibres such as softwood paste (2-5 mm); fibres from leaves such sisal (1.5-3 mm) and abaca (2-7 mm) and cotton linters (2-10 mm) have traditionally been used [9, 10]. However, recently, research into nanosize reinforcements such as cellulose nanofibres has been intensified. The main reason for the use of nanosized fibres is the great reinforcing effect due to the high Young's modulus of the cellulose crystallites. Thus, the disintegration of cellulose fibres can lead to high crystalline nanofibres with a Young's modulus of about 138 GPa and tensile strength of 7.5 GPa [11]. Most applications of cellulose nanofibres have been in reinforcing polymer matrices but, to our knowledge, they have never been applied in cement mortar matrices.

In this work, the performance of ductile cement mortar composites reinforced with cellulose fibres from conventional pulps of sisal and cellulose nanofibres prepared by the application of a high intensity refining process has been evaluate. To improve the composite degradation, silica fume has replaced partially the portland cement. In addition, the effect of a decrease of sand particles in the performance of the material has been evaluated.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1. Materials

UNE-EN 197-1:2000 Type I cement supplied by Ciments Molins (Spain) was used for the present research work. Silica fume has been used to replace a 30 wt.% of the cement. The sand was supplied by Sibelco and a part was subjected to grinding with a Ball mill in order to analyze the effect of the particle reduction in the performance of the composites. Figure 1 shows the particles' size distribution of the milled sand and the as received one compared with cement particles 'size. As seen after the milling process, the sand particles have similar size to the cement ones allowing the formation of a more homogeneous matrix.

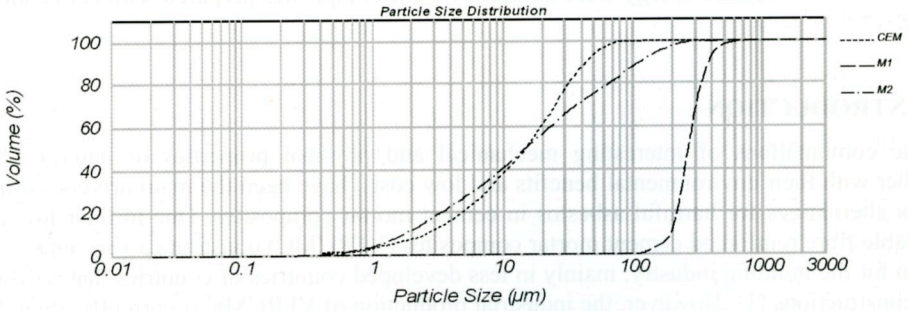

Figure 1. Particle size distribution of the milled sand (M2) and as received sand (M1) compared with the one of cement particles.

Sika Viscocrete-3425 fluidizer, obtained from Sika S.A.U., was used at a maximum dosage rate of 40 g/1000 g of cement to aid workability. Sisal (Agave sisalana) pulp from a soda-anthraquinona cooking process was kindly supplied by a CELESA (Spain).

2.2. Fibre Treatment and characterization

Cellulose nanofibres have been prepared by the application of a high intensity refining process in a Valley Beater. Following the ISO 5264/ 1-1979 (E), 360 grams of oven-dried sisal pulp were added to deionised water, in such a way as to give a final volume of 23 litres, corresponding to a consistency of 1.57 % (m/m). The mixture was placed at the Valley Beater device, where the cut and fibrillation of the sisal fibres took place due to the mechanical action. Different refining times of 1, 2, 3, 4, 5 and 6 hours were studied.

An initial characterisation of the sisal pulp was performed. The fibre dimensions such as length and width were measured according to TAPPI T271 om-02 by using a Kajaani FS300 Analyzer. Measurements were taken from ~5000 fibres. In order to study the intrinsic resistance of the sisal fibres, the zero-span tensile index (ISO 15361:2000) was also determined by using a Pulmac tester. According to ISO 15361:2000 (*E*), the zero-span tensile index (Z_I) was calculated from equation 1.

$$Z_I = \frac{Z_T}{G} \tag{1}$$

where Z_I is the zero-span tensile index (KNm/g); Z_T is the zero-span tensile strength (Kilonewton/meter) and G is the oven-dry grammage (g/m^2). To perform the zero-span test, homogenous isotropic sheets of sisal pulp with a grammage of about 60g/m^2 were produced.

The microstructure and morphology of the sisal pulps obtained at different refining times were analysed by scanning electron microscopy (SEM), using a JEOL JSM-S610 microscope at an accelerating voltage of 10 kV. Prior to examination, a little amount of pulp was diluted in deionised water and an aliquot of this suspension was dropped on a metallic support surface and dried in an oven overnight at 80°C. Finally, the dry pulp surface was sputtered with a thin layer of gold to make them conductive.

2.4. Composite preparation and characterization

In order to study and compare both the reinforcing effect provided by the incorporation of the sisal microfibres and nanofibres and the effect of sand particle's various composites were prepared following the same procedure described previously [9]. Table 1 shows the composition of the samples studied.

Table 1. Reference and composition of the prepared cement mortar composites

Sample reference	Sand type	Fibre treatment	Fibre percentage (wt.%)	Cement/SF/sand proportions (by weight)	Water/Cement ratio
M1SC	Coarse	Conventional pulp	3.5	0.7:0.3:1	0.63
M1SN	Coarse	Nanofibrillated pulp	3.4	0.7:0.3:1	0.84
M2SC	Fine	Conventional pulp	3.1	0.7:0.3:1	0.94
M2SN	Fine	Nanofibrillated pulp	3.3	0.7:0.3:1	0.89

Prismatic specimens were prepared for the flexural tests. The mould used was a UNE-EN 196-1:2005 type with internal dimensions of 40x40x160 mm^3 modified to allow the compression of the specimens to 20 mm of thickness. The specimens were cured for 28 days at 20 ± 1 °C and 95% relative humidity. Three point bending tests were performed using an Incotecnic press equipped with a maximum load cell of 30 kN at a load speed of 50 ± 10 N/s.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF THE FIBRES

Table 2 shows the results of the physical and morphological characterization of the sisal pulp as received.

Table 2. Physical characterization of sisal fibers

Length (mm)	Width (μm)	Aspect ratio (length/width)	Z_l (KNm/Kg)
1.14	15.9	71.4	130±12

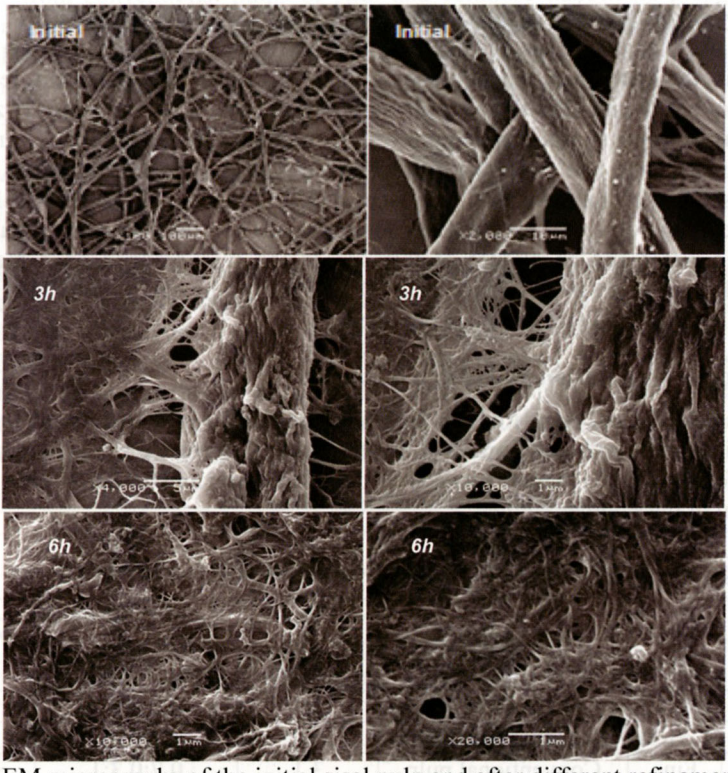

Figure 2. SEM micrographs of the initial sisal pulp and after different refinement times.

Figure 2 shows the microstructure of the initial sisal fibres (first row), and of the pulps obtained after 3 (second row) and 6 (third row) hours of refining at low magnifications (left) and high magnifications (right).

As shown in Figure 2, initially, the sisal fibres have a diameter ranging from 10 to 20 μm, which confirms the sisal average width measured by Kajaani (Table 2). After 1h of refinement, the fibres remain almost intact, although an initial external fibrillation starts to appear, after which a progressive fibrillation of the fibres can be observed. After 3 hours of refinement, the external fibrillation of the fibres can be clearly observed. An increase of the refining time to 4 hours involves an enhancement of the fibrillation degree of the fibres. The initial fibre diameter is reduced to ~5 μm as a consequence of the fibrillation of the outer layers that creates branches in the fibre, leading to the formation of nanofibrils, increasing in this way the fibre specific surface area. Further refinement (6 hours, bottom) yields highly branched fibres in the nanometer scale, between 25 and 250 nm. These nanofibres present a higher intrinsic strength than the initial fibres. This fact, together with the increase of the aspect ratio, could enhance the reinforcing capabilities of these pulps, making them potentially suitable for the production of composites. Moreover, their high specific surface area would potentially favour the interaction with the matrix, giving place to a better stress transfer. Taking into account all these issues, the optimum refining time was found at 6 hours and this pulp was selected for the preparation of the cement composites.

3.2. Mechanical performance of the cement composites

The main parameters obtained from the flexural tests are compiled in Table 3 and the typical bending curves for the specimens analyzed are presented in Figure 3.

Table 3. Mechanical properties of the cement composites prepared

Reference	Sand type	Fibre treatment	Flexural modulus (GPa)	Flexural strength (MPa)	Fracture energy (J)
M1SC	Coarse	Conventional pulp	5.9±0.1	12.9±0.5	431±18
M1SN	Coarse	Nanofibrillated pulp	6.5±0.3	13.1±0.3	78±8
M2SC	Fine	Conventional pulp	5.6±0.8	13.2±0.3	372±17
M2SN	Fine	Nanofibrillated pulp	9.0±0.7	14.0±0.4	348±47

A shown in Figure 3 (left), when the coarse sand is used a slight improvement of both the flexural modulus and strength can be observed for the composites reinforced with nanofibres compared to those reinforced with microfibres. Nonetheless, a significant reduction of the fracture energy is also observed. As previously mentioned, the reinforcing effect of nanofibres is expected to be higher than that of microfibres since the formers present higher intrinsic strength. Moreover, the high specific surface area of the nanofibres results in an enhanced fibre-matrix interaction which involves a better stress transfer from the matrix to the nanofibres. On the other hand, probably due to the finesse of the cellulose nanofibres with respect to the matrix particles the toughness of the composite is not improved.

Nevertheless, for the composites prepared with the fine sand a significant improvement of both flexural modulus and strength without any significant reduction of the fracture energy

can be observed for the composites reinforced with nanofibres compared to those reinforced with microfibers (Figure 3 –right-).

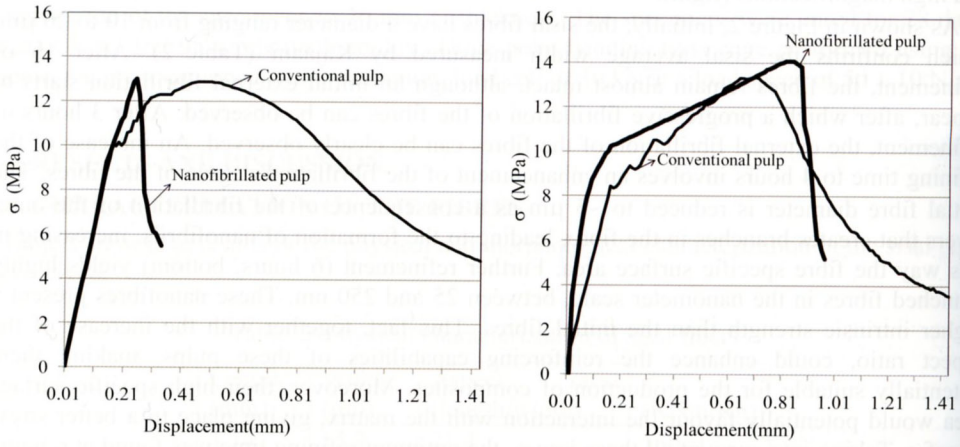

Figure 3. Typical stress versus displacement curves of the composites prepared with the as received sand (left) and the ones prepared with the milled sand (right).

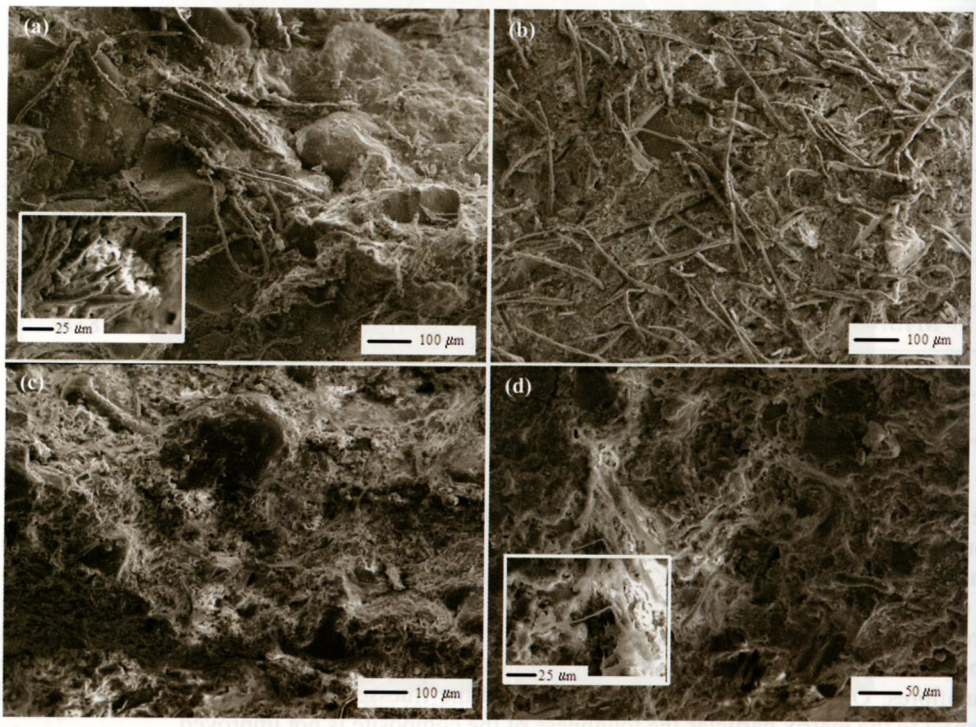

Figure 4. SEM micrographs of the fracture surface of the composites: (a) M1SC; (b) M1SN; (c) M2SC and (d) M2SN.

Concerning to the morphology of the composites, as may be seen in Figure 4a for the ones prepared with the coarse sand and with the conventional sisal pulp, the fibers are concentrated in the zone of the cement paste while the sand zones are almost clean. These aggregates could lead to fracture surfaces linked only on the cement zones. Moreover, there are not observed many pores in the cement paste, which could indicate a good adhesion between the fibers and the cement paste, it is to say, the broken fibers (detail of Figure 4a) remain adhered to the matrix after the fracture process. When the fine sand is used, the fibers appear homogeneously dispersed in the matrix (Figure 4b).

For the composite prepared also with the coarse sand but using the nanofibrillated pulp (Figure 4c), it seems that the fibers and cement form a homogeneous paste surrounding the sand. In this case, as expected from the bending curve, the fibers seem to increase the modulus of the matrix but their lower size does not allow that they act as link after the cracking of the matrix, which leads to a significant decrease of the fracture energy. Nevertheless, when the fine sand is used, the composite is more homogeneous (Figure 4d). Moreover, it is possible to observe cellulose microfibrils (detail of Figure 4d).

4. CONCLUSIONS

In this study, ductile cement mortar composite materials reinforced with nanofibrillated cellulose fibers have been prepared and characterized in order to analyze the potential reinforcement effect of these fibers compared with that of conventional ones. The effect of a decrease of sand particles in the performance of the material has also been analyzed.

The composites prepared with nanofibrillated cellulose and coarse sand exhibit slightly higher flexural modulus and flexural resistance and significantly lower toughness than those prepared with conventional pulps. Nevertheless, the composites prepared with nanofibrillated cellulose and fine sand posses similar toughness, but significantly greater flexural modulus and flexural resistance than those prepared with conventional pulps.

These results confirm the higher potential reinforcement effect of the cellulose nanofibers with respect to the microfibers. Moreover, based on the results of the mechanical testing and microstructural characterization, it can be concluded that in order to obtain cement mortar composites with high modulus and resistance as well as high toughness it could be interesting to combine both, cellulose nanofibers and microfibers.

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