

Wet/Dry Cycling Durability of Cement Mortar Composites Reinforced with Micro- and Nanoscale Cellulose Pulps

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A combination of reinforcements at different levels can have a synergetic effect on the final properties of a composite. The aim of this work was to produce, evaluate, and compare the wet/dry cycling durability of the exposure of cement composites reinforced with conventional pulps at the micro-scale level, with nanofibrillated cellulose fibers at the nano-scale level, and with combinations of both reinforcements (hybrid composites). To evaluate the durability of their mechanical properties, the composites were tested under flexural loading after 28 days of humidity chamber curing and after 20 wet/dry accelerating aging cycles. Composites reinforced with the nanofibrillated cellulose exhibited significantly higher flexural strength and flexural modulus, but they had lower fracture energy values than those reinforced with conventional sisal fibers. Moreover, the hybrid composites with a high content of nanofibrillated cellulose maintained or even improved their properties after aging.

Keywords: Nanofibrillated cellulose; Cement mortar composites; Mechanical performance; Durability

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INTRODUCTION

The use of cellulosic fibers as reinforcements for cement composites represents an interesting option for the building industry (Tonoli *et al.* 2009, 2010; Silva *et al.* 2010; Claramunt *et al.* 2011). These fibers provide adequate stiffness, strength, and bonding capacity to cement-based matrices for the substantial enhancement of their flexural strength, toughness, and impact resistance. However, two main drawbacks restrict the performance of the material: (1) the maximum weight content of cellulosic fibers that can be incorporated into the composites in the form of short fibers (about 8 to 10 wt%), and (2) the long-term durability of the composite.

Concerning the first drawback, the problem is the agglomeration of the fibers during the mixing with the cement. Even using the Hatschek methodology, which allows a good dispersion of the fibers, the maximum content described in references is around 10 wt.%. On the other hand, for higher contents of 6 to 8 wt.% of pulp fibers, although there is an increase of the toughness, the strength and modulus are not improved (Savastano *et al.* 2001) (Claramunt *et al.* 2013). One possible alternative for increasing the reinforcement capacity of the fibers without increasing their percentage content above 6 to 8 wt.% is to use the fibers at the nanoscale level. It is well-known that the reinforcing capability of fibers can be increased by reducing their size to the nanometer scale. Nanofibrillated fibers

can be obtained from vegetable fibers by subjecting them to mechanical, chemical, or enzymatic treatments. These fibers, which consist of alternating crystalline and amorphous domains, have a high specific area and an extensive hydrogen-bonding ability (Eyholzer *et al.* 2009; Lavoine *et al.* 2012).

Research related to nanofibrillated cellulose in polymer composites is widespread (Reddy *et al.* 2013). However, to our knowledge, research related to the use of these fibers as reinforcements in cement mortar matrices is scarce (Ardanuy *et al.* 2012).

The durability problem of cellulose cement composites is associated with an increase in fiber fracture and a decrease in fiber pull-out, which is caused by a combination of weakening of the fibers by alkali attack, fiber mineralization caused by the migration of hydration products to lumens and porous spaces, and volume variation caused by their high water absorption. This causes a reduction in the post-cracking strength and toughness of the material (Savastano and Agopyan 1999; Roma *et al.* 2008). The problem of the presence of calcium hydroxide can be overcome by modifying the composition of the matrix in order to reduce or remove this alkaline compound (Toledo Filho and England 2003; Mohr *et al.* 2007). The problems of the dimensional changes induced by moisture changes are a consequence of the composition of the vegetable fibers, which have a cellulose structure and other hydrophilic components with an affinity for water, thus favoring its penetration into the amorphous regions of the fibers. Various treatments have been used to minimize this problem, such as subjecting the fibers to previous water heating and drying treatments (Claramunt *et al.* 2011; Ferreira *et al.* 2014) or modifying the surface of the fibers to make them more hydrophobic (Tonoli *et al.* 2009). One of the advantages of using nanofibrillated cellulose is that higher dimensional stability is expected since the cellulose microfibrils have high tendency to bond with each other reducing the swelling and cellulose accessibility (Pönni *et al.* 2012). Moreover, as the nanofibrillated fibers will be mixed with the cement matrix dispersed in water, it is expected a better dispersion than in non-polar matrices, where the main problem is the agglomeration of the pulp (Eyholzer *et al.* 2009; Abdul Khalil *et al.* 2014).

The aim of this work was to produce, evaluate, and compare the durability to wet/dry cycling exposure of cement composites reinforced with conventional pulps at the microscale level, nanofibrillated cellulose fibers at the nanoscale level, and combinations of both reinforcements. For this purpose, composites reinforced with nanofibrillated cellulose were assessed and compared with those reinforced with conventional cellulose fibers and combinations of both reinforcements. The mechanical performance of these composites was tested under flexural loading after 28 days of humidity chamber curing and after 20 wet/dry accelerating aging cycles.

EXPERIMENTAL

Materials

UNE-EN 197-1:2000 Type I cement supplied by CIMENCAT (Spain) was used as a cement matrix. Based on previous studies, silica fume was used to replace 10 wt% of the cement (Fernández-Carrasco *et al.* 2014). The sand used, “quartz flour,” Hispania U-S500, has a similar particle size distribution to the cement and was supplied by Sibelco (Spain). Sika Viscocrete-3425 fluidizer, obtained from Sika, Spain, was used at a maximum dosage rate of 40 g/1000 g of cement to aid workability.

Sisal (*Agave sisalana*) pulp from a soda-anthraquinone cooking process was kindly supplied by CELESA (Spain).

Methods

Nanofibrillated cellulose was prepared by the application of a high-intensity refining process in a Valley Beater. Following the ISO 5264/1-1979 (E), 360 g of oven-dried sisal pulp were added to deionized water in such a way as to give a final volume of 23 L, corresponding to a consistency of 1.57% (m/m). The mixture was placed in the Valley Beater device, where the cutting and fibrillation of the sisal fibers took place as a result of the mechanical action. A refining time of 6 h was used (Ardanuy *et al.* 2012). The microstructure and morphology of the pulps were analyzed by scanning electron microscopy (SEM) in a Jeol JSM 6400 (USA).

In order to study and compare the reinforcing effect provided by the incorporation of the sisal microfibers and nanofibers, as well as the combination of both reinforcements, five series of composites were prepared following the same procedure described previously (Ardanuy *et al.* 2012). Cement/silica fume/sand proportions (by weight) for all the composites were 0.9:0.1:1. Table 1 shows in detail the composition of the samples prepared. To prepare the components, firstly a dispersion of water, fluidizer, and nanofibrillated pulp is prepared by mixing mechanically. The water content used corresponds to the final mixture of water/cement ratio equal to 1. Then cement and sand are mixed with the dispersion of the fibers. Finally, the mixture is divided in 3 equal portions which are pressed in the molds at 4.5 MPa for 24 h. During the first minutes of the compression process, samples lose the excess water. The final w/c ratio depends on the characteristics of the mixture, being higher for the composites with higher content of nanofibrillated pulp.

Table 1. Reference and Composition of Prepared Cement Mortar Composites

Sample Reference	Conventional Pulp (wt%)	Nanofibrillated Pulp (wt%)	Water/Cement Ratio
1	8	0	0.69
2	6	2	0.65
3	4	4	0.63
4	2	6	0.59
5	0	8	0.56

Rectangular solid specimens were prepared for the flexural tests. The mold used was UNE-EN 196-1:2005 with internal dimensions of $40 \times 40 \times 160 \text{ mm}^3$, modified to allow the compression of the specimens to a 10-mm thickness. After demolding, the specimens were cured for 28 d at $20 \pm 1 \text{ }^\circ\text{C}$ and 95% relative humidity. Three-point bending tests were performed using an Incotecnic press equipped with a maximum load cell of 3 kN and controlled by the cross-head displacement at a rate of 2 mm/min. The modulus of elasticity (MOE) and the flexural strength were calculated following the Standard UNE-EN-12467 and the fracture energy following the TFR4 test of RILEM “The determination of energy absorption in flexure of thin fiber reinforced cement sections”. The composite durability was estimated with accelerated aging tests, a methodology widely used to study the degradation of vegetable fibers in cement matrices (Toledo Filho and England 2003; Mohr *et al.* 2005). For this purpose, half of the specimens prepared for each series were

subjected to 20 wet/dry cycles after curing. The wet/dry cycle used was 96 h of soaking in water at room temperature followed by 72 h of drying in an oven provided with open air circulation at 60 °C (Claramunt *et al.* 2011). To characterize the fiber-matrix interface, the fracture surface of the composites was observed using a JEOL JSM-S610 microscope at an accelerating voltage of 10 kV. A focused ion beam (FIB) was also used to resolve the nanofibrillated pulps.

RESULTS AND DISCUSSION

Characterization of Nanofibrillated Cellulose

Figure 1 shows the microstructure of the initial sisal pulp and of the pulps obtained after 6 h of refining.

As Fig. 1 shows, initially the sisal fibers had a diameter ranging from 10 to 20 μm in width. Six hours of refinement yielded highly-branched fibers on the nanometer scale, between 25 and 250 nm. The increase in the aspect-ratio could enhance the reinforcing capabilities of these pulps because their high specific surface area favors interaction with the matrix, giving way to a better stress transfer (Tonoli *et al.* 2007; Ardanuy *et al.* 2012).

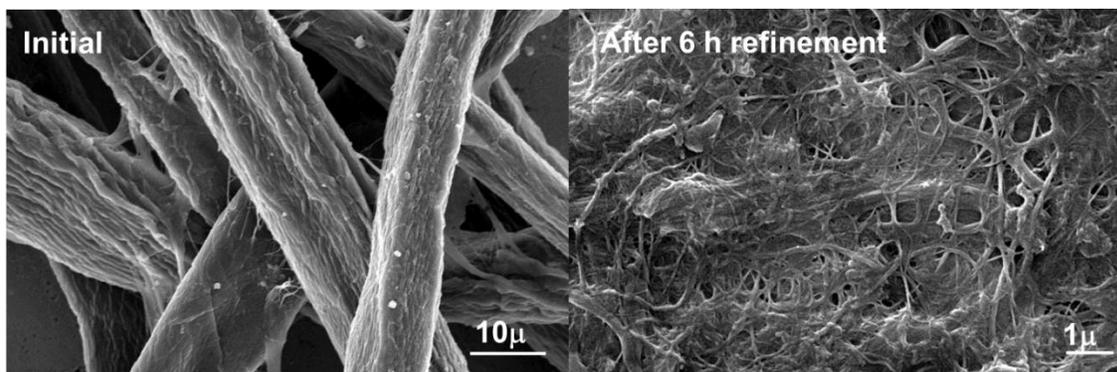


Fig. 1. SEM micrographs of the initial sisal pulp (2,000x) and sisal pulp after 6 h refinement (10,000x)

Characterization of the Cement Mortar Composites

The typical bending curves obtained from the flexural tests for the specimens tested after 28 days of curing are depicted in Fig. 2, and the main parameters obtained from these curves are presented in Table 2.

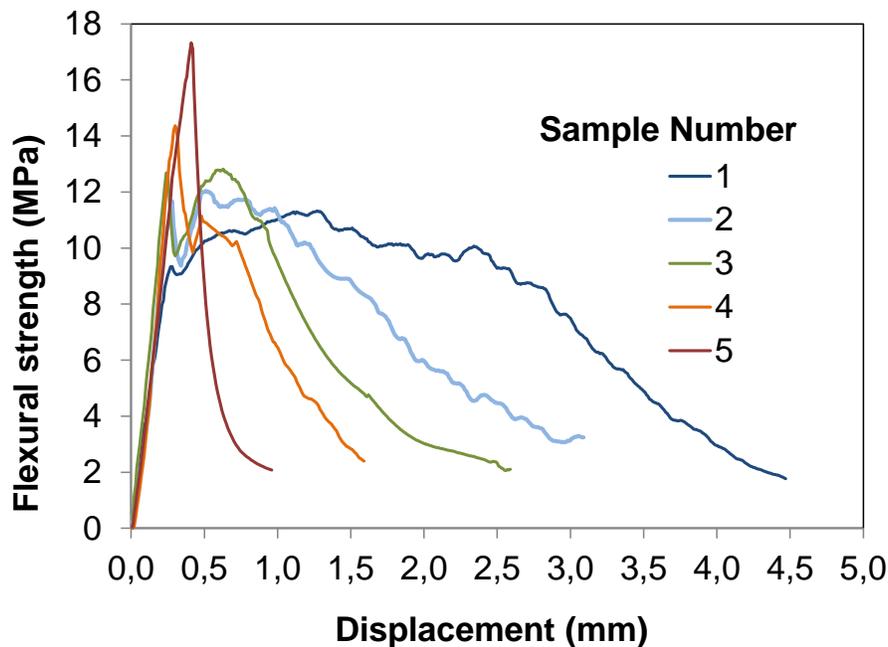


Fig. 2. Typical stress *versus* displacement curves of the composites prepared with nanofibrillated cellulose (sample 5), conventional pulp (sample 1), and combinations of both reinforcements (samples 3, 4, and 5)

As shown, the values for maximum flexural strength increased with increasing nanofibrillated pulp content. This behavior can be attributed to the increased interaction between the nanofibers and the matrix, which is promoted by the increase of the aspect-ratio caused by the high fibrillation of the fibers. When the fiber-matrix interaction degree increases, there is a decrease in the interface matrix deformation, which increases the shear stress and thus the maximum tensile strength of the composite. Higher modulus of elasticity (MOE) values were also obtained for the composites with higher contents of nanofibrillated pulp. The highest modulus was achieved for the composite with a combination of reinforcements with proportions of 6% nanofibrillated pulp and 2% conventional pulp.

Table 2. Mechanical Properties of Cement Mortar Composites

Reference	Flexural Strength (MPa)	Fracture Energy (kJ/m ²)	MOE (GPa)
1	11.6 ± 0.6	1.514 ± 0.114	3.6 ± 0.4
2	12.0 ± 0.5	0.737 ± 0.047	4.6 ± 0.4
3	13.3 ± 0.5	0.387 ± 0.015	6.9 ± 0.8
4	14.3 ± 0.5	0.244 ± 0.009	7.7 ± 1.2
5	15.9 ± 1.2	0.143 ± 0.011	5.6 ± 0.4

The toughness of the composites decreased with increasing nanofibrillated pulp content and exhibited more brittle behavior, as can easily be deduced from the small plastic area in the stress-displacement curve and from the fracture energy value. As previously reported by Ardanuy *et al.* (2012), this brittle failure can be attributed to the low crack bridging capacity of the nanofibrils, since their short length is insufficient to prevent the

growth of matrix microcracks. Unlike the composites reinforced with nanofibrillated cellulose, those reinforced with conventional sisal pulp exhibited a more plastic behavior, since long fibers are more effective in bridging the crack faces. In addition, the interfacial properties of these composites are weaker as a consequence of the low fiber specific surface area, favoring toughening by debonding and fiber pull-out. This effect is illustrated in Fig. 3. In the samples with 8 wt% of conventional pulp (Fig. 3a), it can be observed as a fracture surface with a matrix connected by a fiber network, with a high content of fiber pull-out, which hence generates considerable energy losses that contribute to an increase in toughness. However, for the samples with high contents of nanofibrillated pulp, the fracture surface presents few cracks and roughness. The low presence of long fibers and the lower friction of the fracture are related to the higher stiffness of the composite.

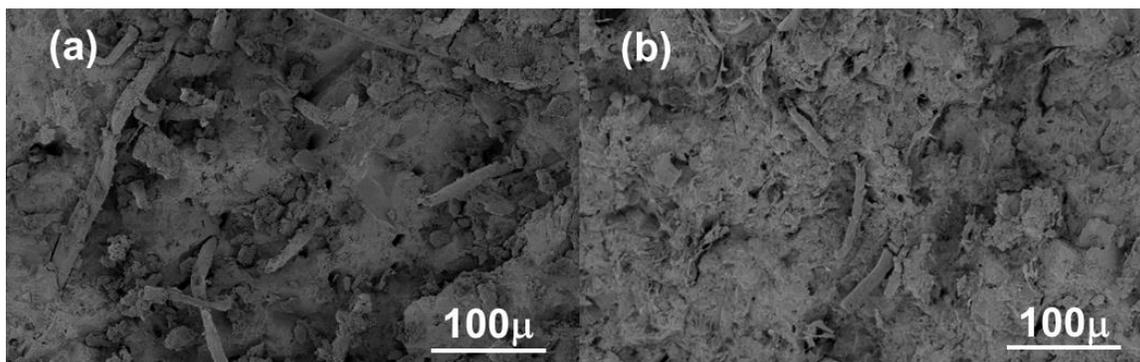


Fig. 3. SEM of the fracture surface of composite reinforced with 8 wt% (250x) of (a) conventional pulp (reference sample 1) and (b) nanofibrillated pulp (reference sample 5)

On the other hand, an increase in matrix stiffness with increasing load was observed. This means that for a load of less than 4 MPa, the slope of the curve is lower than for higher loads (between 4 MPa and the maximum value). This effect was more significant for the compounds with a high content of nanofibrillated pulp, as shown in Fig. 4. This embrittlement of the composite with high loads was attributed to an embrittlement of the matrix at the nanostructure level. The greatest increase in stiffness was observed for composites with 6 wt% of nanofibrillated pulp combined with 2 wt% of conventional pulp. The properties of this material could be of interest for applications where low deformation with high stress is necessary. Moreover, the percentage of the conventional pulp contributes to an increase in the toughness of the material.

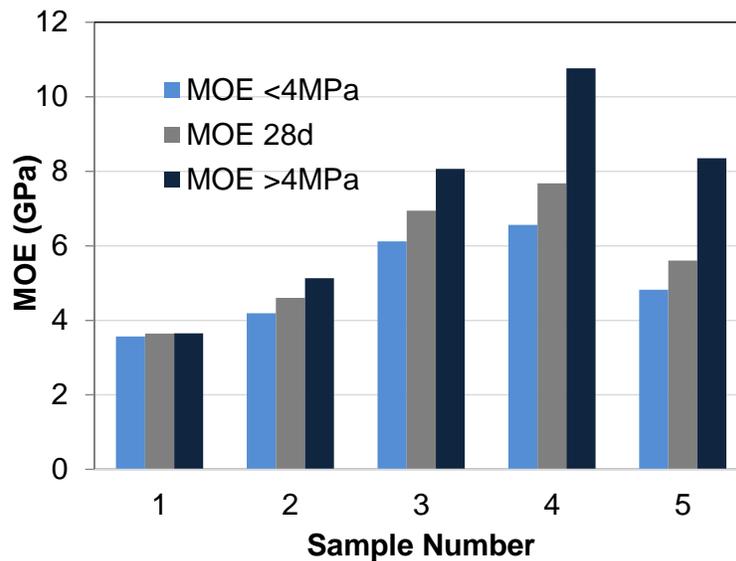


Fig. 4. MOE values calculated for the reference samples 1 to 5 for strengths higher than 4 MPa and lower than MPa, compared with average MOE values

Concerning the evaluation of the durability of the composites, Fig. 5 shows the variation of the values of the flexural modulus and flexural strength with aging. As shown and in general after aging the samples, the flexural modulus increases. This embrittlement can be explained by two different effects, depending on the composition of the composites. For composites with a high content of conventional pulp, this behavior is related to the mineralization of the fibers, and thus to an embrittlement of the composite (Mohr *et al.* 2005; Tonoli *et al.* 2007). For composites with a high content of nanofibrillated cellulose, this can be attributed to a densification of the interfacial zones. As previously mentioned, a higher interaction between the nanofibrillated pulp and the matrix led to composites with significantly higher flexural strength (Fig. 6a). Moreover, unlike the composites with a high content of conventional pulp, an increase in flexural strength with aging was observed for composites with nanofibrillated pulp. This behavior is related to an increase in fiber-bonding caused by the attachment between the two phases by the effect of aging, which is a consequence of the densification of the interfacial zones combined with a strong interaction between both phases. Figure 6b confirms the strong interactions between the nanofibrillated cellulose and the matrix, with the cement particles (C-S-H particles) intermixed with the nanofibers.

Nevertheless, for composites reinforced with the conventional pulp, hygroscopic changes in the fibers led to detachments between the two phases and hence a decrease in their tensile strength, as previously observed for similar composites (Mohr *et al.* 2005; Tonoli *et al.* 2007; Claramunt *et al.* 2011).

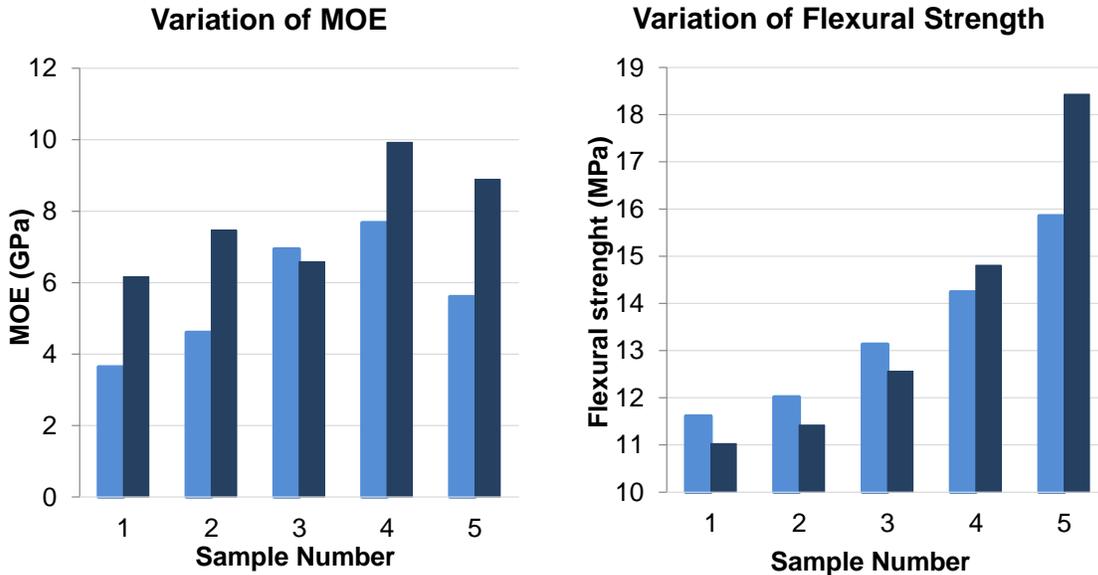


Fig. 5. MOE and flexural strength values for composites (reference samples 1 to 5) cured at 28 days (light color) compared with aged ones (dark color)

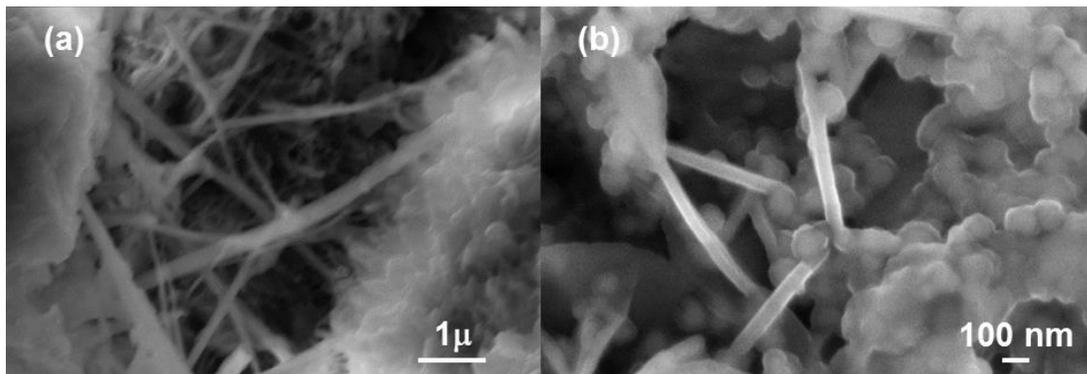


Fig. 6. BSEM of the fracture surface of composite reinforced with 8 wt% of nanofibrillated pulp (a) detail of nanofibrillated cellulose intermixed with cement matrix particles –unaged composite– (40,230x) and (b) detail of the dispersion of fibers on the matrix (141,890x) –aged composite–

As expected, the fracture energy of the conventional composites was greatly decreased by aging as a consequence of fiber-debonding and mineralization. However, the composites with nanofibrillated pulp presented similar or even improved fracture energy after aging (Fig. 7).

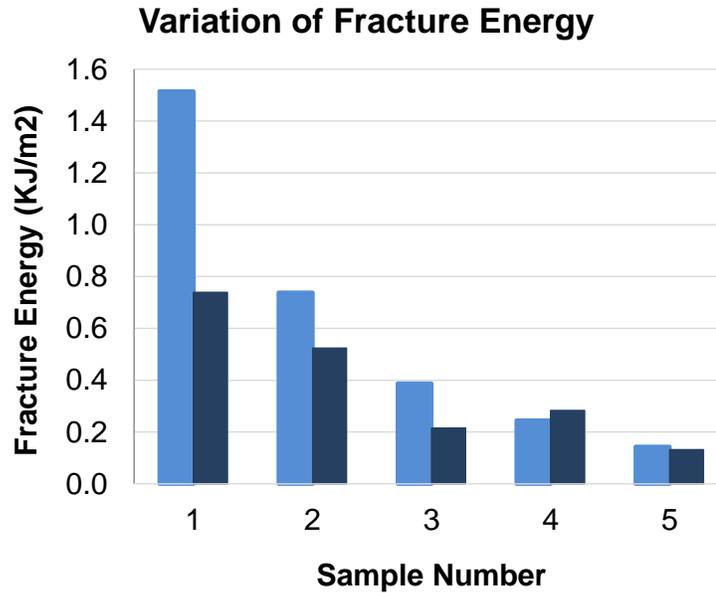


Fig. 7. MOE and flexural strength values for composites (reference samples 1 to 5) cured at 28 days (light color) compared with aged ones (dark color)

CONCLUSIONS

1. The cement mortar composites reinforced with the nanofibrillated cellulose exhibited significantly higher flexural strength and flexural modulus values, lower values of fracture energy, and improved durability over composites reinforced with conventional sisal fibers.
2. The MOE of composites with nanofibrillation increased at high loads (higher than 4 MPa), and this effect was more significant for compounds with higher contents of nanofibrillated pulp.
3. Composites with low contents of nanofibrillated cellulose fibers (less than 4 wt%) exhibited lower flexural strength and fracture energy values after aging. Composites with high contents of nanofibrillated cellulose fibers (4 wt% or more) had higher flexural strength, maintaining their fracture energy after aging.

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