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Nanomontmorillonite Reinforced Fibre Cements and Nanomontmorillonite-Nanosilica Reinforced Mortars

Styliani PAPATZANI[1]
Kevin PAINE[2]

ABSTRACT

In this study the effects of an organomodified nanomontmorillonite (nMt) dispersion (nC2) and of a powder type nMt (nC4), were compared in quaternary low carbon footprint fibre-reinforced cementitious nanocomposites and mortars. 60% Portland cement, 20% limestone (LS) and 20% fly ash plus fibres/superplasticizer comprised the reference paste. nMt was added at 1% by mass. Pastes were investigated in terms of flexural strength, thermal properties, density and water impermeability. Neither of the two types offered strength enhancement. nC2 showed some potentials at late ages (90 days). Thermal gravimetric analyses showed limited additional pozzolanic activity towards the production of additional C–S– H at day 90, in agreement with flexural strength results and X-ray diffraction analysis, which showed the consumption of $Ca(OH)_2$ even at day 28. No change in density was observed, whereas water impermeability tests showed that nC2 was more effectively organomodified not allowing water to be absorbed neither in the short nor in the long term, while nC4 at later ages seemed to be absorbing water back. Lastly, cubes of mortars were prepared and tested in compression in an attempt to fully investigate the potentials of the formulations. The effect of using simultaneously nMt and nanosilica (nS) was also recorded, however no increase in compressive strength was observed. The long-term density of the mortars was also investigated, results suggesting poor compaction which was not adjusted with the use of admixtures. These results are in support of previous studies undertaken in the field, showing that the purpose of use of organomodified nMt's must be clearly defined before any formulations are designed.

Keywords: Organomodified nanomontmorillonites, fibre cements, nanomontmorillonite and nanosilica enhanced mortars, characterization.

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1 University of West Attica, Department of Surveying and Geoinformatics Engineering, Aigaleo, Greece
Hellenic Army Academy, Department of Mathematics and Engineering Sciences, Attika, Greece
spapatzani@uniwa.gr - spapatzani@sse.gr - https://orcid.org/0000-0001-8475-8975

2 Centre for Innovative Construction Materials University of Bath, Department of Architecture and Civil Engineering, Bath, England
k.paine@bath.ac.uk - https://orcid.org/0000-0001-7455-7002

1. INTRODUCTION

Under the European Union FP7 project (FIBCEM), different nanomontmorillonite (nMt) dispersions were produced by the project partners and tested in cementitious binders at the University of Bath, in an effort to produce low carbon footprint cements specifically for fibre cement applications [1,2]. Despite the availability of alternative cementitious systems [3–5], the carbon footprint of fibre cements is typically lowered by reducing the Portland cement content in binary combinations [6,7], as analytically reviewed elsewhere [8]. However, the downside to this is lower early-age strength and often lower long-term strength at the low water to cement (w/c) ratio required for manufacture. A potential solution to this is to use nanoparticles to nucleate and enhance the hydration processes, thus, in effect improving and maximising the cement hydration reactions [9–11]. The authors of the current paper have carried out exhaustive investigations on the level of CO_2 reduction that is technically achievable by minimizing Portland cement content and simultaneously, increasing the content of cement additions such as limestone, fly ash or silica fume in a number of different reference formulations, typical of the requirements for fibre cements [8], whilst trying to maintain performance through rational use of nanoparticles. In the process of finding the upper and lower limits of nanoparticle inclusion in these composite formulations, potential synergies amongst the constituents were determined, as well as antagonistic functionalities through a number of studies on different materials' combinations [8]. For example, in high fly ash content formulations, it was found that the inclusion of nanosilica did not exhaust the $Ca(OH)_2$ produced during the hydration of cement, but there was plenty of $Ca(OH)_2$ available for further reactions, given time. In fact, a direct correlation was observed between the $Ca(OH)_2$ available at different ages of curing with the compressive strength of the pastes.

In the research above, three nMt dispersions were compared, investigating their effectiveness in cementitious binders. In a recent publication, for the first time one organomodified dispersion (nC2) and the inorganic dispersion (nC3) were compared against an industrial product, of undispersed nanomontmorillonite in powder form (nC4) [12]. The reference formulation was a non-pozzolanic paste containing 60% PC, 40% LS, 3% PVA fibers and 2% superplasticizer. Furthermore, results on the effect of the undispersed nMt, nC4 in comparison with results on the effect of nC2 on flexural strength and crystallographic characteristics were presented in a pozzolanic reference paste containing 60%PC, 20%LS, 20%FA, 3% PVA fibres and 2% superplasticizer [13].

Further studies by other scientific teams have yielded promising results and have shed more light on the effect of nMts in cementitious matrices; for example it has been proven that cement pastes containing organomodified nanomontmorillonite possess damping properties, a result that can potentially alter the dynamic response of structures made by this material offering a more sustainable option for damping [14]. Moreover, it has been established that the cation exchange degree of nMts having the same modifier, affects the chemical reactivity of the nanoparticles and the lower it is the sooner the nanoparticles of montmorillonite can engage in pozzolanic reactions and the higher the mechanical properties measured [15]. In a subsequent study, four different nMts were synthesized with a modifier with and a modifier without aromatic substitute group and four different basal spacing (d_{001} by X-ray diffraction measurements) [16]. Cementitious nanocomposites were formulated with these four nMts additionally containing colloidal nanosilica with superplasticizing properties and tested. It was concluded that the aromatic substitute group lead to larger d_{001}, and this structural change lead to enhanced hydration of the paste at earlier ages, signaling higher mechanical strength and considerably lower sorptivity, while strength development was almost unaffected by basal spacing. Very recently it was shown that another parameter that must be taken into consideration is the chain length of the surfactant, which was proven to affect the morphology of the cement nanocomposite and the mechanical strengths [17]. Only 0.5% addition of nMt lead to over 11% increase in compressive strength due to the filling and nanoreinforcement effect of the nMt. Furthermore, the pozzolanic activity of a bentonite clay, modified by silane was found superior even to calcined bentonite clay by quantifying portlandite consumption transforming into additional calcium silicate hydrates with the help of thermogravimetric and Rietveld analyses [18]. The additional advantage of this modification was that the swell index and hydrophilicity of the nanobentonite was considerably reduced. In a subsequent study the authors showed that silane treatment can successfully reduce the hydrophilicity of sodium montmorillonite up to 84% [19].

Following the strategy of previous research carried out by the authors, the carbon dioxide footprint of the formulations under consideration was limited in a twofold manner; (i) the amount of Portland cement was reduced beyond the acceptable by the Eurocodes limit and (ii) the amount of supplementary cementitious materials (SCM) was increased, again beyond the acceptable by the Eurocodes limit (Figure 1)[20]. To leverage possible delay in hydration reactions nanoparticles of montmorillonite have been added as SCM and nanoreinforcement in the resulting fibre cement nanohybrids. Therefore, the present study offers a complete overview of the microstructural and thermal changes the addition of similar nMt's can attribute to a pozzolanic reference paste, depending on their state (dispersed or in powder form).

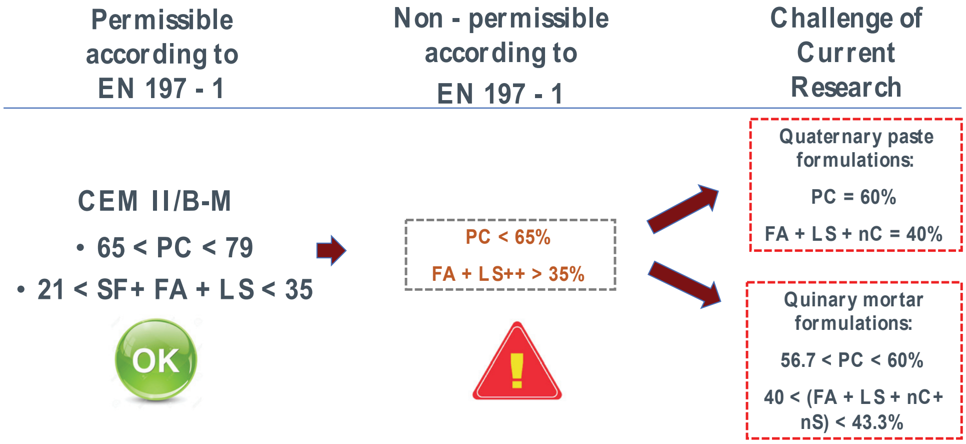

Figure 1 - Eurocode limits of clinker substitution and supplementary cementitious materials (SCM) addition and target of current research.

These new results on thermal properties, relative density and impermeability, that largely affect the microstructure and strength gain of cementitious nanocomposites are correlated with crystallographic results already presented [21]. Lastly, for the first time, compressive strength and long term density of mortar cubes has also been tested in an effort to solidify the conclusions made with respect to pastes. In fact, the addition of nanomontmorillonite has been stretched by the additional inclusion of nanosilica, which has been found particularly effective in strength gain in previous research. This final paper of the extensive analysis of nanomodified pastes in ternary, quaternary or even quinary low Portland cement content formulations, contains the additional attempt for further activation of the nMt's by adding nanoparticles of silica (LnS) in the mortar mixes.

2. MATERIALS AND METHODS

2.1. Materials and Nanomaterials

The materials and nanomaterials used were:

- Portland limestone cement CEMII/A-L42.5 (containing 14% by mass of limestone). The supplier gave the following clinker composition: 70% C_3S, 4% C_2S, 9% C_3A, 12% C_4AF.
- Limestone (additional - LS), conforming to EN 197-1. The total LS content of each paste was the sum of that contained in the Portland limestone cement and this additional LS.
- Fly ash (FA), conforming to EN 450. The oxide composition provided by the material data sheet was: 53.5% SiO_2, 34.3% Al_2O_3, 3.6% Fe_2O_3, 4.4% CaO.
- Organomodified nanomontmorillonite (nMt), nC2 dispersed in water with the help of an alkyl aryl sulfonate surfactant, containing about 15% by mass of nMt particles.
- Organomodified nanomontmorillonite (nMt), nC4, a commercially available product by Sigma-Aldrich, undispersed – in powder form. It consists of Montmorillonite K-10 (70-75%) surface modified with 25-30WT% methyl dihydroxyethyl hydrogenated tallow ammonium (Nanomer® I.34MN). The supplier's data sheet gives the following additional information: $6.5<pH<7.0$ and density = 1.7 g/cm^3. It should be noted that, the specific industrial product used has been discontinued recently.
- Commercially available colloidal amorphous nS containing 15% by mass of nanoparticles in an aqueous suspension (LnS).
- PVA fibers, kuralon H-1, 4 mm added at 3% by weight.
- Superplasticizer viscocrete 20HE, denoted as SP.

The levels of embodied CO_2 have been agreed in the UK and are evaluated in terms of kg CO_2 per tonne of binding material [22].

- PC = 930 kg CO_2/ tonne
- FA from coal burning power generation = 4 kg CO_2/ tonne
- LS = 32 kg CO_2/ tonne

It can be seen that in terms of CO_2 footprint, the use of FA as a supplementary cementitious material is beneficial. This is the reason for which it was used in the paste design despite of its shortage in the UK. The main goal of this research was to produce low carbon footprint cements. This was achieved by the following concept as also thoroughly explained utilizing Figure1: First of all PC, which is the most polluting material, was reduced below European Standard EN 197 -1 [23] acceptable limits and LS and FA were added above EN 197 -1 acceptable limits simultaneously. Moreover, of the available nanoparticles for cement scientists, the organomodified or inorganic nanoparticles have been produced by the naturally available material clay, by extracting the montmorillonite fraction and then a chemical (surfactant and/or modifier) is used. For the particular nMt's the platelets are not separated with calcination as with the calcined nanoclays [24] and therefore, nanohybrids of the above constituents present the lowest possible of embodied CO_2, even though the exact number of embodied CO_2 for the nanoparticles has not been assessed for the nMt nanoparticles.

2.2. Characterization of Constituent Materials and Nanomaterials

Particle size distribution analysis with optical system can provide the PSD of a wide range of scales of particles from 10 nm to 3 mm. Particle size distribution analysis was carried out at the MANIT laboratory, Bhopal, India, using a Laser Scattering Particle Size Distribution Analyzer Horiba LA950. Results are typical for this type of industrially available materials, as can be seen in Table 1 [20].

Table 1 - PSD results of materials [20].

	Mean size (μm)	Mode size (μm)	Median size (μm)	Diameter at 10% (μm)	Diameter at 90% (μm)
CEMII	11.38	2.74	3.25	1.40	22.16
LS	12.14	2.44	3.21	1.36	31.89
FA	9.09	2.14	2.53	1.46	10.13

The organomodified nanomontmorillonite nC2 was analyzed via X-ray diffraction (XRD), showing a d-spacing of 3.95 nm at 2.2°2θ and 2.0 nm at 4.4°2θ. Transmission electron microscopy (TEM) imaging revealed platelets ranging in size of 50-300 nm [25].

The commercial nanomontmorillonite had a particle size ≤ 20 micron but was also characterized before introduced to cement pastes. XRD analysis yielded a d-spacing of 1.8 nm which is more than expected for unmodified nanomontmorillonite. Transmission electron microscopy imaging showed platelets reaching the size of 100-300 nm [26].

The particles of nanosilica (nS) were characterized by means of TEM and SEM/EDX [13] and by Fourier transform infrared spectroscopy [27] by the authors in previously published research. They were found to be spherical with a diameter ranging from 8 nm to 50 nm. The LnS particles were homogenously dispersed in water and highly concentrated.

The characterization of the two organomodified nMt's via XRD, TEM, scanning electron microscopy coupled with X-ray energy dispersive spectroscopy and thermal gravimetric analyses (TGA) carried out in previously published research [12] has shown the following:

- TEM analyses showed that the production process for nC4 produced less crystalline structures.
- The XRD analysis of nC4 yielded a basal spacing (d-value) of 1.8 nm, which is more expected in unmodified nMt. nC2 seemed to have both intercalated (presence of higher order reflection which are typical of regular stackings) and exfoliated (disappearance of peak at 19.7 °2θ) platelets.
- Compared to nC2, the commercially available nC4 was better exfoliated, but showed marginally greater variation in Si/Al and more polycrystalline phases.

2.2. Methods

2.2.1. Formulation of nMt and Fibre Reinforced Cementitious Nanohybrids

Following previous research, the PC content was kept constant and the content of nMt solids was deducted from the LS content. By doing so, the $Ca(OH)_2$ production during PC hydration was comparable in all pastes, in order to detect potential additional pozzolanic activity due to the addition of nMt's [12]. The reference formulation comprised 60%PC, 20%LS, 20%FA, 3% PVA fibres and 2% superplasticizer, was denoted as F.PC60LS20FA20PVA3SP2 (F is for flexure) and was enhanced by the addition of nMt.

The formula for the nMt-fibre reinforced quaternary matrix was:

$$PC\ (60) + LS\ (20\text{-}x) + FA\ (20) + PVA\ (3) + SP\ (2) + xnMt \quad (1)$$

Where x = % of nMt solids.

The different concentrations of the nMt dispersions are shown in Table 2. Only the 1% concentration was implemented, as it was found optimal in previous studies [8,12,28]. The amount of 2% superplasticizer was tested in previous research [12] and was found to be ideal in ternary formulations which also contained fibres and nMt, therefore the quaternary ones also started off with 2% superplasticizer. The water to solids ratio was kept constant for all formulations at 0.3.

Table 2 - Composition of quaternary fibre cement nanohybrids - proportions % by total mass of solids.

Sample Annotation	PC (%)	LS (%)	FA (%)	nMt (%solids)	SP (%)	PVA (%)	W/S
F.PC60LS20FA20PVA3SP2+0%nMt	**60**	**20**	**20**	**0.0**	**2**	**3**	**0.3**
F.PC60LS39PVA3SP2 +1%nC2	**60**	**19**	**20**	**1.0**	**2**	**3**	**0.3**
F.PC60LS39PVA3SP2 +1%nC4	**60**	**19**	**20**	**1.0**	**2**	**3**	**0.3**

A consistent mixing procedure has been followed for the entire project under which the current research is presented and has been already published by the authors [29]. The steps include:

- Dry mixing of all powder components was firstly carried out with a spatula by hand.
- For formulations containing nMt, the nC1 or nC2 nC3 dispersion was poured in a separate container together with water, stirred with the use of a magnetic stir bar for 1 min and then added to the mixed powders.
- The PVA fibres were added last after they had been manually further separated.
- With the addition of water (and nC2/nC4 where applicable), the paste was mixed employing a dual shaft mixer at 1150 rpm for a duration of up to four minutes.
- Slabs of 120 × 40 mm and 10 mm thickness were produced.

2.2.2. Formulation of nMt and nS Reinforced Mortars

A number of standard mortar cubes were also tested in compression in a final effort to explore any possible improvements within the new matrix (M.PC60LS20FA20), as shown in Table 3. The formulations were prepared in an automatic mixer complying with EN 196-1 mixing times. The w/b ratio was equal to 0.5, according to the standard and no superplasticizer was used. Distilled water and standard sand were used. The proportions by mass according to the standard were: one part of the cement, three parts of CEN Standard sand, and one half part of water (water/binder ratio 0.50). Each batch for three test specimens consisted of:

- (450 ± 2) g of powders (PC/LS/FA/nMt solids)
- (1 350 ± 5) g of sand and
- (225 ± 1) g of water

nC2 dispersion was diluted in the calculated amount of distilled water that was needed for every mortar combination.

nC4 being in powder form was dry mixed with other constituents in powder form (PC, LS and FA) and then water was added.

Table 3 - Composition of quaternary and quinary mortars - proportions % by total mass of solids.

Sample Annotation	**PC (%)**	**LS (%)**	**FA (%)**	**nMt (%solids)**	**nS (%solids)**	**w/b**
M.PC60LS20FA20+0%nMt	**60**	**20**	**20**	**0.0**	**0.0**	**0.5**
M.PC59LS20FA20+1%nC2	**59**	**20**	**20**	**1.0**	**0.0**	**0.5**
M.PC58LS20FA20+2%nC2	**58**	**20**	**20**	**2.0**	**0.0**	**0.5**
M.PC57.5LS20FA20+2%nC2+0.5%LnS	**57.5**	**20**	**20**	**2.0**	**0.5**	**0.5**
M.PC58.6LS20FA20+1.4%nC4	**58.6**	**20**	**20**	**1.4**	**0.0**	**0.5**
M.PC57.2LS20FA20+2.8%nC4	**57.2**	**20**	**20**	**2.8**	**0.0**	**0.5**
M.PC56.7LS20FA20+2.8%nC4+0.5%LnS	**56.7**	**20**	**20**	**2.8**	**0.5**	**0.5**

Each mortar formulation was cast into the standard moulds (160 x 40 x 40 mm), in three layers. It was vibrated and covered for 24 hours. Samples were demoulded and kept into water at 20±2ºC thereafter until the day of testing. On the day of testing (at day 7, 28, 56 and 90), cubes of 40 x 40 x 40 mm were cut from the prisms with a diamond saw at a very low speed to avoid cracking.

2.3. Characterization

2.3.1. Characterization of nMt and Fibre Reinforced Cementitious Nanohybrids and Mortars

The testing methodology comprised the following:

Flexural (three-point bending) strength tests were carried out in accordance with BS EN 12467. Flexural strength tests were carried out in accordance with BS EN 12467. Mean strength values of three specimens were calculated, as well as standard deviation at 7, 28, 56, and 90 days. All samples were tested at a loading speed of 0.5 MPa/s on a 100 kN servo hydraulic testing machine.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (dTG) were carried out using Setaram TGA92. Each powder sample was placed in an alumina crucible and heated at a rate of 10 ºC/min from 20 to 1000 ºC in nitrogen atmosphere, as explained above for the characterization of nC4 at day 7, 28, 56, and 90. Buoyancy effects were taken into account, by correcting the curves using automatic blank curve subtraction. For the paste characterization, arrest of hydration was performed following two different methodologies: oven drying and solvent exchange. For TGA/dTG, the oven drying technique was adopted.

Three different areas were distinguished, as described in the literature, and correspond to the hydrates produced and consumed [29]:

i) The first area is related to the dehydration of C–S–H, ettringite, gehlenite and monosulfate, between 100◦C and 200◦C.

ii) The second area of interest is associated with the dehydration of $Ca(OH)_2$ between 440◦C and 510◦C.

iii) The third area of interest is the decomposition of $CaCO_3$ occurring between 700◦C and 810◦C.

For the late age relative density measurements, BS EN 12390-7:2009 [23], was selected as a basis and the exact procedure followed is covered in literature [29]. Mean density values of three specimens were calculated, as well as standard deviation.

Water impermeability tests were based on BS EN 492:2012 but the test was modified to account for the much smaller specimens used in this research (slabs 120 × 40 mm and 10 mm thickness). A transparent tube of 250 mm length was used as the water column with an internal bore of 29 mm diameter. A control water column was also adopted to ensure zero water evaporation in the laboratory testing environment. Tests were carried out at 7, 28 and 56 days.

2.3.2. Characterization of nMt and nS Reinforced Mortars

Compressive strength tests of mortars were carried out on three 40 mm cube specimens per mix [30]. All samples were tested at a loading speed of 0.5MPa/s. The compressive strength reported comprised the mean of the three results.

Long-term relative density of mortars was carried out in accordance with BS EN 12390-7:2009, which is designated for hardened concrete with limitations on the maximum coarse aggregate size, was selected as a basis for the long-term relative density measurements of the mortars. The volume of the specimen was obtained by water displacement because this method is suitable for specimens of irregular shape.

3. RESULTS & DISCUSSION

3.1. Results of nMt and Fibre Reinforced Cementitious Nanohybrids

3.1.1. Flexural Strength

As shown in Figure 2, nC4 provided marginal strength improvement at early ages, which, however, showed a reduction in strength at later ages (90 days). Although the standard deviation for the reference paste ranged was similar to the nC2 modified samples, for nC4 it was much lower and equal to about 0.8 MPa. This evidence of better distribution of nC4 in the mass of the paste did not offer strength improvements and therefore it has been postulated

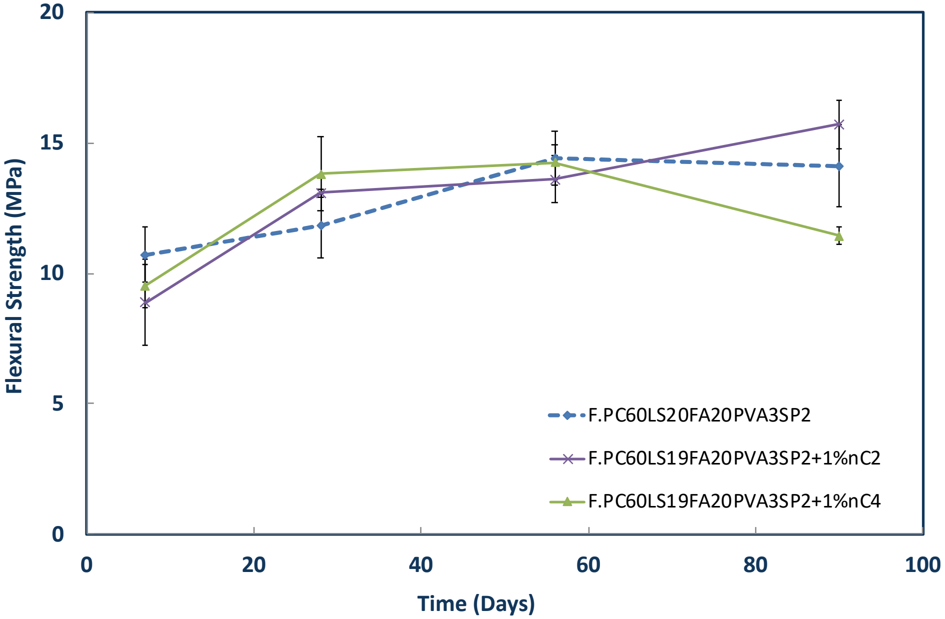

Figure 2 - Flexural strength of 1% nC2 and nC4 fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2 [21].

that for cementitious nanohybrids it is best to disperse the nMt in water [21]. Moreover, with respect to nC4, the two events together; i.e. the significant error and the strength drop at later ages lead to the understanding that the specific commercial product is unstable in cement formulations. This conclusion is drawn by the fact that the reduced basal spacing of 1.8 nm, as discussed in section 2.1 above relates more to unmodified montmorillonite rather than modified one. It is possible, hence, that not all the platelets are individually available for reactions, as it should be the case. As a result, the commercial product is less reactive as a nanomaterial compared to nC2, that was produced for the scope of the FIBCEM project.

3.1.2. Thermal Gravimetric Analyses

For the fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2, similar results to the ones based on F.PC60LS20FA20PVA3SP2 can be observed (Figure 3A and Figure 3B). Lastly, sample F.PC60LS19FA20PVA3SP2+1%nC4 seems to have carbonated, a condition that could be attributed to the fabrication process of the nMt and the properties this process yielded.

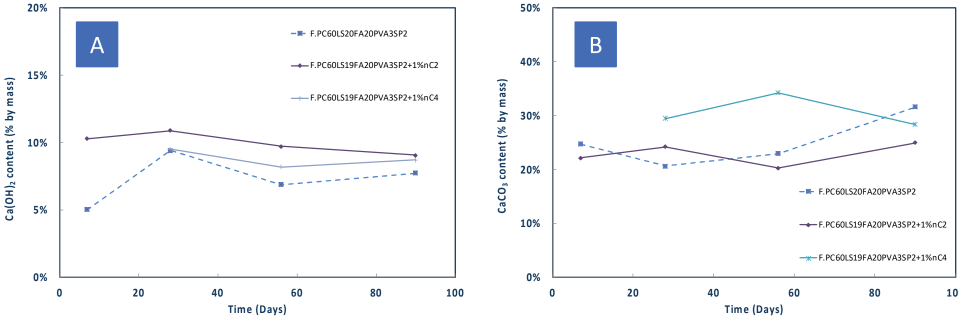

Figure 3 - Effect of nMt type on (A) $Ca(OH)_2$ and (B) $CaCO_3$ content of fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2.

The pozzolanic performance was evaluated by TG analyses between approximately 100-180°C, at day 7, 28, 56 and at day 90 for the two different nMt types. As shown in Figure 4, at day 28 no additional C–S–H was produced neither by nC2 nor by nC4. By day 90 nC2 produced greater quantities of ettringite and C–S–H. However, sample F.PC60LS19FA20PVA3SP2+1%nC4 seems to have carbonated, therefore, the consumption of $Ca(OH)_2$ cannot be exclusively attributed to the production of ettringite and C–S–H. For this, X-ray diffraction analysis was also carried out at day 28 to assess the consumption of $Ca(OH)_2$ and monitor the amount of $CaCO_3$ present in the formulations, however no additional $CaCO_3$ was detected, whereas $Ca(OH)_2$ was indeed consumed [21].

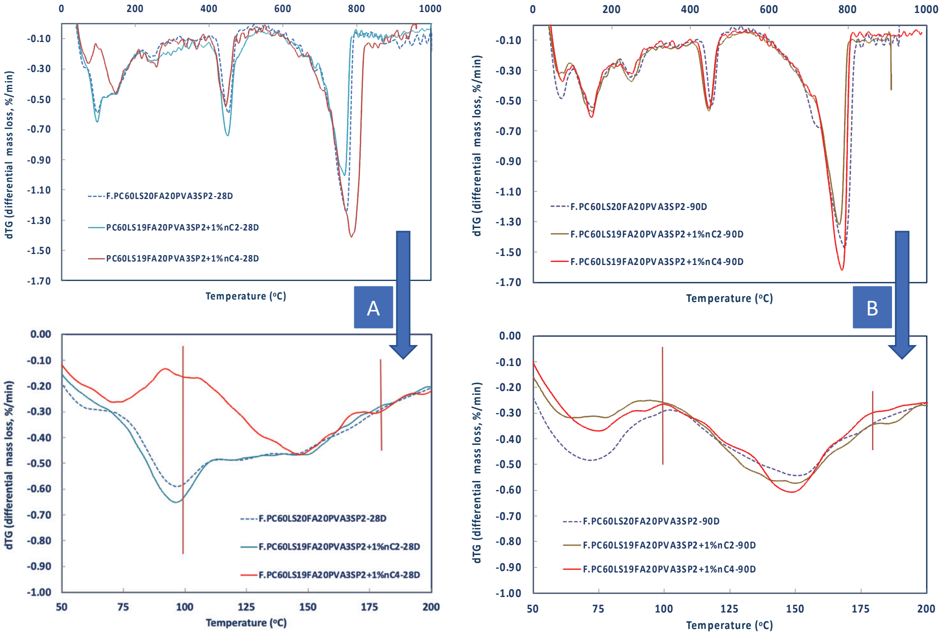

Figure 4 - Differential mass loss between 100-200°C of fibre-cement nanohybrids at (A) Day 28 [21] and (B) Day 90.

3.1.3. Relative Density Analyses

Late age (after month 3), relative density measurements were taken. All measurements showed a very low standard deviation (Figure 5) as in the case of the F.PC60LS40PVA3SP2 nanohybrids [12]. No significant difference between the reference paste and the nC2 or nC4 modified ones was observed and in fact, due to the very low nanoparticle addition no significant changes were expected either.

3.1.4. Water Permeability Analyses

Water impermeability tests were carried out for the fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2, as before. As shown in Figure 6, the organoclays exhibited better performance than the reference nanohybrid at early ages. However, at later ages nC4 seemed to be less impermeable than the reference nanohybrid. These results are directly related to the flexural strength performance, as well, leading to the conclusion that the organomodification create clusters, increase porosity and in total, add localised weaknesses in the volume of fibre-cement nanohybrids.

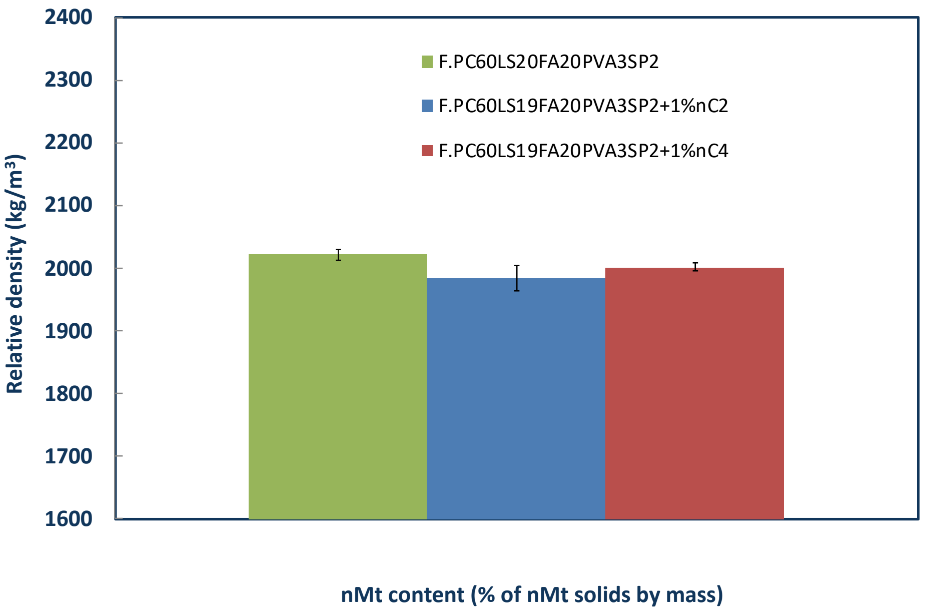

Figure 5 - Effect of nMt type on long term relative density of fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2.

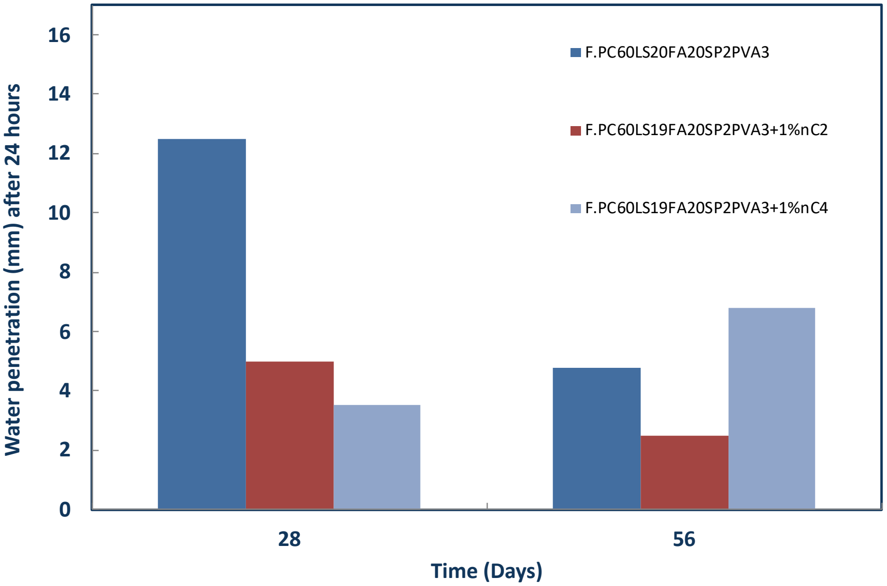

Figure 6 - Effect of nMt type on the impermeability of fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2.

3.2. Results of nMt and nS Reinforced Mortars

3.2.1. Compressive Strength of Mortars Based on PC60LS20FA20

The compressive strength of mortar cubes based on PC60LS20FA20 and denoted as M.PC60LS20FA20 was measured (Figure 7). The standard deviation of the compressive strength remained within 0.5 and slightly increased for the higher nC2 concentrations, as expected since the dispersion was highly viscous. The best performance was achieved for the lower nC4 concentration, followed by the nC4 and nanosilica (nS) modified mortar. nC2 exhibited the lowest compressive strengths, however, best combination was given at 2% nC2 and 0.5% nS addition, as shown in Figure 7. It can also be deducted that nC4 could not be further optimized neither at greater concentrations nor with the addition of nS. The fact that nC4 absorbed water back into the paste could explain the drop of flexural strength at later ages.

It should be noted that the 28-day compressive strength of mortars containing 100% CEMII/A-L42.5 should be near 42.5 MPa. However, the mortar mixes tested contained 56.7 - 60% PC, hence the much lower 28-d compressive strength values. In addition, limestone content is very high 20% and fly ash content is equally very high, 20%, which has been found to delay strength gain beyond 56 days of curing. Although previous research on nanoreinforced pastes has shown that 0.5% addition of nanoparticles is optimum and in some mixes this addition can extend to 1.0%, the aim of this series of trial mortar mixes was to assess if the carbon footprint of the mix can be lowered by reducing the amount of PC and increasing the amount of nMt without compromising the strength. The experience gained by these results leads us to believe that the main difficulty in mortar mixes when using dispersed nMt rather than powder nMt, is to achieve homogeneous scattering of the nanoparticles throughout the matrix. For this, a step further would be to use sonicators for better dispersing nanoparticles within the mixes or nanofluidic droplets for more homogenous mixes [12]. Lastly, it could be argued that the compressive strength loss in the case of mortar application may be attributed to the effectiveness of surfactant in the presence of fine aggregate.

Interestingly, in a study published in 2021, on cementitious nanocomposites containing nMts and nanosilica the following mixing procedure yielded enhanced strength results; colloidal nanosilica with superplasticizing effects was used as dispersing medium. The nMt was poured into the nS suspension and part of the total required water and mixed with a magnetic hotplate stirrer at 1000 rpm for at least one hour. Then the nMt-nS-water suspension was mixed with cement and the residual water was added just before the mixing time was completed [16]. This procedure proved to be very efficient by providing highly dispersed suspensions, which eventually lead to higher observed compressive strength of the nanocomposites.

The issue with homogeneous dispersion of nMt in mortars has indeed attracted scientific attention. Another possible strategy for better dispersion of nMts in mortar matrices has been presented in 2022 [31]; wet grinding of raw montmorillonite in the presence of 1% of Polyethylene glycol for increased layer spacing through intercalation effect and enhancement of grinding efficiency, yielded an increase of 28.6% in one-day flexural strength for 2% nMT addition, although authors noted drawbacks to the later age strength development. More specifically the 28-day flexural strength of the nMt-mortars was similar to the reference mortar, whereas the 28-day compressive strength of the nMt-mortars was lower than the reference mortar. The lower compressive strength at later age was attributed to the lower hydration degree of the higher (1% or 2%) nMt additions according to ^{29}Si NMR analyses. Also mercury intrusion porosimeter analyses showed that at 28 days the nMt enhanced mortars exhibited a larger harmful pore fraction than the reference mortar, a factor possibly contributing to the reduced compressive strength [31].

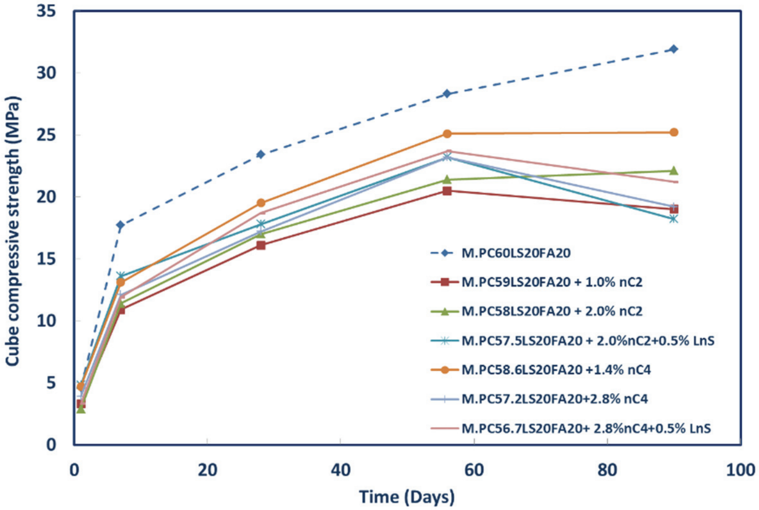

Figure 7 - Cube compressive strength of nC2 or nC4 and LnS modified mortars based on PC60LS20FA20.

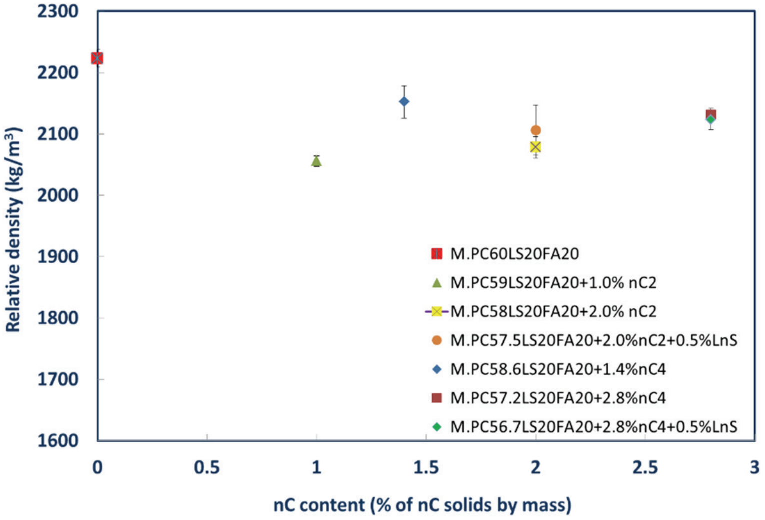

Figure 8 - Long term relative density of nC2 or nC4 and LnS modified mortars based on M.PC60LS20FA20.

3.2.2. Long Term Density of Mortars Based on PC60LS20FA20

The long term (after month 3) relative density measurements of the mortar cubes showed minor variation for nC2 and more significant for nC4 (Figure 8). The closest performance to the reference mortar was achieved by nC4. This is another indication as to why nC4 performed better in compression. The homogenous mixing and the compaction of the samples produced with nC4 was easier, due to the fact that it was added in powder form than in dispersion as nC2. This, possibly led to denser and more homogeneous mortars.

4. CONCLUSIONS

In the current paper, an exhaustive analysis of the addition of two different organomodified nMt's was presented. It was found that the one dispersed in water had better potential for improvement compared to the undispersed industrial product. Although $Ca(OH)_2$ was consumed, minimal amounts of additional C–S–H were identified, which could partially explain the limited strength enhancement. A hypothesis that nMt's act as nanofillers was rejected since there was practically no difference in the long-term density results. Moreover, results of impermeability tests were consistent with non-pozzolanic pastes, showing that nC2 can act as water barrier in pastes [12].

Lastly, the testing of various mortars led to the conclusion that nS can offer further improvements to nMt modified binders. Different compositions of nMt modified cements and mortars can yield significantly different mechanical performances. A possible advancement of the research on mortars could involve the production of samples with the use of nanofluidic droplets for the homogenous dispersion of nMt in the matrix and with lower w/b ratios containing superplasticizers, which are expected to yield interesting results as a number of limitations can be eradicated:

1. More coherent mortars can be delivered.
2. Nanoparticles mobility could be enhanced by avoiding clustering.
3. Minimization of total porosity would be expected.
4. Better pore size distribution should be maintained, since nanoparticles are better dispersed within the mass of mortars.

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