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Interesting Remarks on the Comparison of Organomodified Nanomontmorillonites in Fibre-Cement Nanohybrids

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Abstract. This paper presents the effects of the addition of (i) the organomodified nanomontmorillonite (nMt) dispersion, nC2, produced for the scope of the FP7 project name FIBCEM and of (ii) the powder, undispersed organomodified industrially produced nMt, nC4 on quaternary nMt-fibre reinforced binders. The reference binder consisted of 60% Portland cement (PC), 20% limestone (LS) and 20% fly ash (FA). Superplasticizer was added at 2%, polyvinyl alcohol fibres at 3% and nMt was added at 1%. Flexural strength test were carried out at day 7, 28, 56 and 90 showed marginal enhancement offered by the nMt dispersion, which was attributed to limited, but existing additional pozzolanic reactivity of the particles of nMt. If fact, following methodology presented in published papers on other formulations, thermal gravimetric and X-ray diffraction analysis showed limited consumption of $Ca(OH)_2$ towards production of additional C–S–H, which is in line with the marginal increase of flexural strength for the same age of testing.

1. Introduction

Through a series of publications the effect of nanoparticles on composite cement pastes and binders was investigated [1, 2] in light of the necessity to lower the CO_2 footprint of cementitious composites. The greatest part of these studies covered ternary, quaternary or quinary pastes, which did not include fibres or superplasticizers, whereas two articles have been published on the use of nanomontmorillonites (nMt) on a non-pozzolanic reference formulation (containing Portland cement and limestone) of fibre-cement nanohybrids, which contained Portland cement and limestone [3, 4]. It was found that of the organomodified nMt's the best performing was the one aqueous dispersed in water with the help of an alkyl aryl sulfonate surfactant. The industrial powder nMt, nC4, did not offer any strength, chemical, or microstructural enhancements [4] and the inorganic nMt was presented as a promising nanoparticle [3].

In this work, research is being extended to quaternary formulations. Fly ash is added to the abovementioned cementitious matrix (now containing Portland cement, fly ash and limestone) in an

effort to lower the environmental impact of the reference paste. Then, nMt is added at 1% by total mass of binder, which has been found to be the optimum amount in previous research on cement pastes [5] or on fibre-cement nanohybrids [4]. The focus on this study has been to witness any enhancements of flexural strength by the addition of two different organomodified nMt's and to interpret the strength results with the help of thermogravimetrical and crystallographic findings.
To the best knowledge of the authors, this is the first time that an industrial organomodified powder nMt is compared against an organomodified aqueous dispersion nMt in low PC clinker quaternary fibre-cement nanohybrids.

2. Materials, mix design and methods

2.1. Materials

The materials used were:

- Portland limestone cement CEMII/A-L42.5, with a limestone content of 14%, conforming to EN 197-1. The supplier gave the following clinker composition: 70% C_3S, 4% C_2S, 9% C_3A, 12% C_4AF.
- Limestone (LS) (additional), conforming to EN 197-1.
- 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 nMt, nC2 dispersed in water with the help of an alkyl aryl sulfonate surfactant, containing about 15% by mass of nMt particles.
- Organomodified nMt; nC4 in powder form containing about 15% by mass of nMt particles.

2.2. Mix design

In the present paper a quaternary formulation comprising a pozzolanic reference paste containing 60%PC, 20%LS, 20%FA, 3% PVA fibres and 2% superplasticizer, denoted as F.PC60LS20FA20PVA3SP2 (F is for flexure) is enhanced with nMt. Water content in nMt dispersions accounted for 85%, which entered as part of the water content in the cement formulations to obtain water to binder ratio of 0.3 (or in other words water-to-solids ratio). Therefore, the general formula of the matrix of the resulting ternary nanomodified cement formulations was:

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

Where x = % of nMt solids.
The mixing procedure was standardized by the authors. Pastes were cast in prismatic moulds, producing slabs of the following dimensions: 10 mm depth, 40 mm breadth and 120 mm length (figure 1) and compacted at a shaking table. They were subjected to a 24-hour air-curing and subsequently demoulded and cured in distilled water thereafter at 20±2 ℃ until the day of mechanical testing.

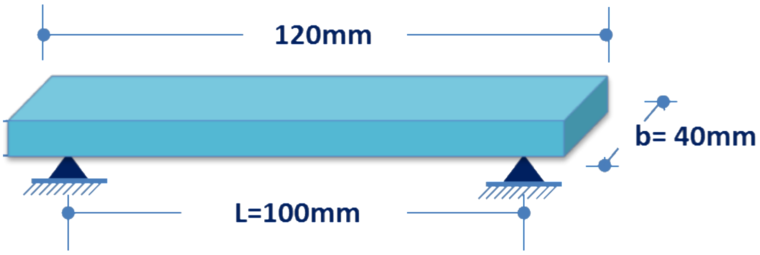

Figure 1. Dimensions of specimens.

2.3. Testing methodology

Flexural (three-point bending) 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 day 7, 28, 56 and 90.

For the TGA/dTG and XRD paste characterization, arrest of hydration was performed following the oven drying technique, as described by Calabria-Holley et al. [6].

Thermogravimetric analysis (TGA) was carried out using a Setaram TGA92 instrument. Approximately 20 mg of nC4 were placed in an alumina crucible and heated at a rate of 10 ℃/min from 20 ℃ to 1000 ℃ under 100 mL/min flow of inert nitrogen gas. The differential thermogravimetric curve (dTG) was derived by the TG curve. The first derivative curve was produced for the various samples tested and was used for comparisons instead of the mass loss curve, as it yields sharp distinctive peaks.

XRD measurements were performed using a D8 ADVANCE X-ray diffractometer with CuKα radiation. Spectra were obtained in the range $4° < 2\theta < 20°$ at an angular step-size of 0.016° 2θ. The state and extent of dispersion - exfoliation of the NMt can be examined by XRD and TEM analysis with monitoring changes in basal spacing [7].

3. Results and discussion

3.1. Mechanical testing

Figure 2 displays the flexural strength of the different specimens. nC4 provided marginal strength improvement at early ages, which, however, showed a reduction in strength at later ages (90 days). What is also worth noting is that the standard deviation for the reference paste ranged from 1 to 1.2 MPa, however for nC2 modified samples, it reached approximately 1.2 MPa, whereas for nC4 it was much lower and equal to about 0.8 MPa. It can, therefore, be postulated that for cementitious nanohybrids it is best to disperse the nMt in water.

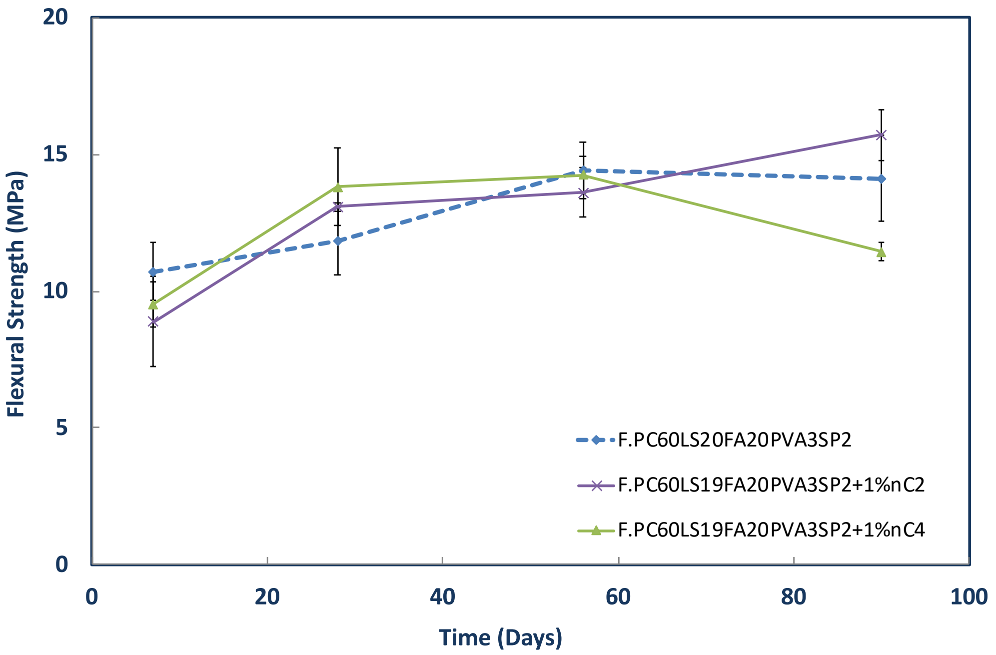

Figure 2. Flexural strength of 1% nC2 and 1% nC4 fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2.

3.2. Thermal gravimetric and X-ray diffraction analysis

As shown in figure 3, at day 28, no additional C–S–H was produced by nC4, whereas the addition of nC2 produced limited quantities of additional ettringite and C–S–H [8]. According to other research results it is expected that as time proceeds, nC2 will consume more $Ca(OH)_2$ towards the production of additional C–S–H [4, 9, 10] .

In addition to this, X-ray diffraction analysis was also carried out at day 28 to confirm the consumption of $Ca(OH)_2$ and monitor the amount of $CaCO_3$ present in the formulations. Indeed, as shown in figure 4, the $Ca(OH)_2$ present in the reference paste was consumed with the addition of nMt. Again there is a high correlation between the $Ca(OH)_2$ consumed and the flexural strength [5, 8]. nC4 at day 28 seems to have delivered the highest flexural strength and has also consumed the greatest amount of $Ca(OH)_2$ although from the analysis between 100 – 180 ℃ no additional C–S–H was produced.

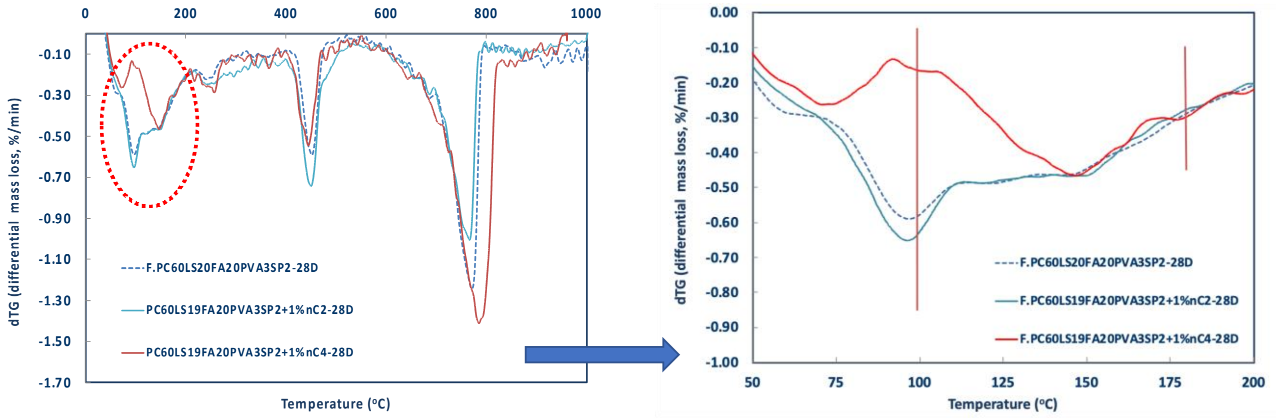

Figure 3. Differential mass loss between 100-200 ℃, at day 28 of fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2.

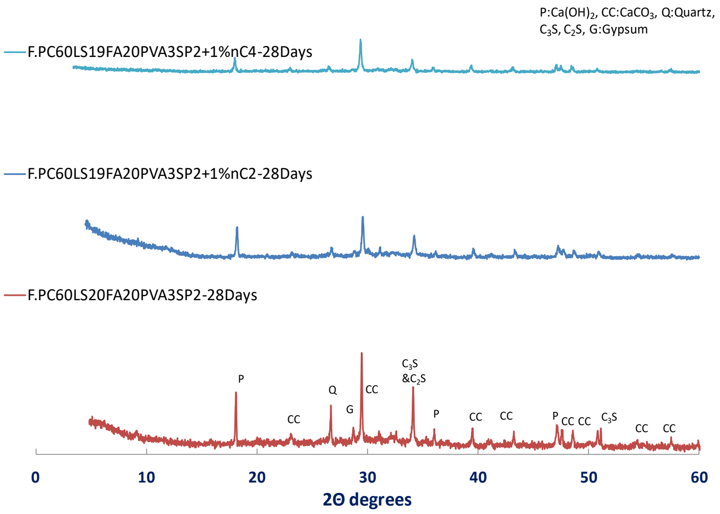

Figure 4. XRD pattern at day 28 of fibre-cement nanohybrids based on F.PC60LS20FA20PVA3SP2.

4. Conclusions

The effects of the addition of two completely differently produced organomodified nanomontmorillonites was assessed in terms of flexural strength. Results were correlated with the consumption of $Ca(OH)_2$ although limited production of additional C–S–H was attested. The overall consensus is that nMt performs better if dispersed in water, when cementitious nanocomposites are produced.

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