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Pore-Structure and Microstructural Investigation of Organomodified / Inorganic Nano-montmorillonite Cementitious Nanocomposites

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Abstract. In the present paper, the effect of three different types of nano-montmorillonite dispersions (nMt) on the (i) microstructure as witnessed by Scanning Electron Microscopy, (ii) long term density measurements and (iii) pore structure as determined via Mercury Intrusion Porosimetry of Portland – limestone cement formulations have been compared, in an effort to determine the upper and lower bound of nMt addition in cementitious nanocomposites. The reference formulation, contained 60% PC and 40% LS by mass of binder aiming at the minimization of clinker and maximization of other constituents. Two aqueous organomodified NMt dispersions (one dispersed with non-ionic fatty alcohol and the other with anionic alkyl aryl sulphonate) and one aqueous inorganic NMt dispersion (dispersed with sodium tripolyphosphate) were added at 0.5, 1, 2, 4 and 5.5% by mass of solids as replacement of Portland cement. The water to solids ratio was kept constant at 0.3. The inorganic nMt showed the greatest potentials for microstructural enhancement. The way in which the level of the nMt platelet separation affected the pastes was discussed. The research reported was part of a much broader project supported by the EU.

INTRODUCTION

The need to lower cement clinker is more pronounced as ever, given the efforts for CO₂ footprint reduction (e.g. Europe 2020 strategy, Global Energy Efficiency and Renewable Energy Fund and others). At the same time the emergence of nanotechnology has allowed the formulation of cementitious composites beyond regulatory acceptable limits. Latest findings have ascertained the increase in mechanical strengths and pozzolanic reactivity with the addition of nanoparticles [1], the good affinity of nano-montmorillonite (nMt) particles in pH environments as that of hydrating cement [2] and the overall effect nanotechnology can have on the detection and investigation of cement's binding agent, C–S–H [3]. One of the challenges of this study was to create a Portland-composite binder with high limestone content and lower than the permissible clinker content according to EN 197-1 [4], by adding nanoparticles of montmorillonite. Indeed, for CEMII/A-L cements, the allowable clinker content falls within 80-95% by mass of binder and the permissible limestone content is limited to 6-20%. In this research three different aqueous nanomontmorillonite dispersions were used; (i) the first was dispersed with non-ionic fatty alcohol and was

called nC1, (ii) the second (nC2) was dispersed with anionic alkyl aryl sulphonate and (iii) the third one (nC3), the inorganic nMt dispersion was dispersed with sodium tripolyphosphate. The process of the nMt platelet separation by using different modifiers and different dispersants and the difference between the organomodified and inorganic dispersions has been described elsewhere [1], [5]. Characterization of the three dispersions via TEM imaging and crystallography, XRD, SEM/EDX and TGA/DTG also taking into consideration results published in cement pastes lead to the following conclusions [6]:

- In nC1 the platelets were not exfoliated, and were possibly re-agglomerating in cement paste. This re-agglomeration may lead to increase in porosity and reduction in density of nC1 added formulations due to the void creation. Such results were expected to worsen with increase in the nC1.
- In nC2, platelets were partially exfoliated and better dispersed in water, still presenting areas of weakness due to limited but existing re-agglomeration of particles.
- Lastly, the nanostructure of nC3 revealed exfoliated platelets, well dispersed in the aqueous dispersion. Better particle packing and reduced porosity is expected with the addition of nC3.

The research presented herein was designed to assess these hypotheses by investigating the performance of the three different nMt dispersions in Portland-limestone cements of low clinker. The methods selected included long term-relative density measurements of pastes containing 5 different nMt percentages, Mercury Intrusion Porosimetry (MIP) of the best performing dosage at different ages and lastly back-scattered scanning electron imaging at late ages to determine possible correlation with long term- relative density.

MATERIALS, MIX DESIGN AND METHODS

Materials

The materials used were:

- Portland limestone cement CEMII/A-L42.5, with a limestone content of 14%, conforming to EN 197-1.
- Limestone (LS) (additional), conforming to EN 197-1.
- Organomodified nMt; nC1 in an aqueous dispersion containing about 15% by mass of nMt particles.
- Organomodified nMt; nC2 in an aqueous dispersion containing about 15% by mass of nMt particles.
- Inorganic nMt; nC3, in an aqueous dispersion containing about 15% by mass of nMt particles.

Mix design

Fifteen ternary cement combinations were generated by using Portland cement, limestone, and either of the two organomodified nMt dispersions or the inorganic nMt dispersion. The reference paste, named PC60LS40 contained only Portland limestone cement (PC) and additional limestone (LS) (PC60LS40 accounting for 60% Portland cement - PC and 40% Limestone – LS). The nMt addition ranged from 0%, 0.5%, 1%, 2%, 4% to 5.5% by mass of solids. The 5.5% represented the upper limit of nanoclay addition in the cement paste. 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:

$$60PC + (40 - x)LS + xnMt \quad (1)$$

Where $x = \%$ of nMt solids at ranges from 0 to 5.5%.

The mixing procedure was standardized as in the case of research on nanosilica particles presented by the authors [7]; dry constituents were pre-mixed for 60 seconds, then, the liquid phases, water and nC dispersion, were added and mixed with an automatic dual shaft mixer at 1150 rpm for 3 minutes. Samples of the fresh pastes were separately for MIP, density and microstructural analyses. Specimens were air cured in dry sealed conditions at $20 \pm 2^\circ\text{C}$ for the first 24 hours, then in water at $20 \pm 2^\circ\text{C}$, until the day of testing.

Methods - Characterization techniques employed

To characterize the pastes, arrest of hydration was performed following two different methodologies as described by Calabria-Holley et al.[8]. A set of SEM images was collected for the reference paste and for the 1% addition of nC1, nC2 and nC3, at day 90. Samples were imaged using a Jeol 6480 LV SEM. A backscattered electron detector was used to capture images of the as received, uncoated, samples.

Long-term relative density measurements for the pastes were taken in accordance with BS EN 12390-7:2000. Volume was obtained by water displacement.:

$$V = \frac{m_a - m_w}{\rho_w} \quad (2)$$

Where, m_a = the mass of the specimen in air, in kg, m_w = the apparent mass of the immersed specimen in water, in kg, ρ_w = the density of water, at 20 °C, taken as 998 kg/m³.

$$D = \frac{m_a}{V} \quad (3)$$

Where, D is the relative density in kg/m³.

Lastly, porosity at the nanolevel was investigated by MIP. The mercury intrusion porosimeter used was an Autopore III - Model unit 9420 supplied by Micromeritics, Hexton, Herts, UK. Stems of 3 ml capacity were filled with solids of the arrested hydration paste.

RESULTS AND DISCUSSION

The reference paste and the 1% nMt modified pastes were examined with the help of SEM. PC60LS39+1%nC1 (Figure 1 – B1&2) was the less dense of the three nanomodified pastes with many crystals, spikes and unhydrated PC particles present. In addition, significant microcracks and voids could also be distinguished in the micrograph of the nC1 modified paste. PC60LS39+1%nC2 (Figure 1 – C1&2) showed a denser, fibrillar structure with layers in parallel probably created by the nC acting as seeding agents for the hydration products. In this micrograph, Ca(OH)₂ crystals and ettringite spikes are also present whereas PC60LS39+1%nC3 (Figure 1 – D1&2) seemed to be the densest of the three with a honeycomb structure and less visible crystals and spikes. However, even at day 90 unhydrated cement particles could be identified (enclosed in rectangles).

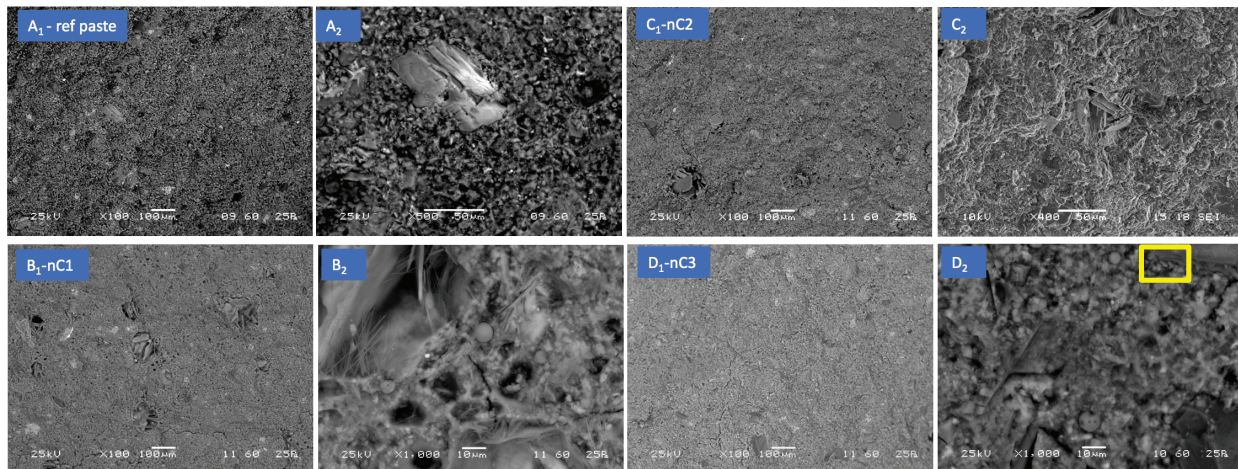


FIGURE 1. Back Scattered electron image at 90 days of (A1) PC60LS40 @ 100x and (A2) @ 500x. (B1) of PC60LS39+1%nC1 @ 100x and (B2) @ 1000x. (C1) of PC60LS39+1%nC2 @ 100x and (C2) @ 400x. (D1) of PC60LS39+1%nC3 @ 100x and (D2) @ 1000x.

Late age density measurements were taken of the nMt modified pastes. All measurements showed a very low standard deviation. As can be seen in Figure 2-A, nC1 exhibited lower densities as the amount of nMt solids increased. The fact that even the lowest nMt addition caused a significant reduction in density could only be attributed to the poor compaction during production, resulting in a less dense paste, and possibly in an increase in the porosity. Adding to this, the characterization of the nC1 dispersion showed re-agglomerating particles, causing areas of potential weakness in pastes [5]. Hence, in this way, the low compressive strengths delivered by the nC1 addition [6] can be justified. nC2 showed a better performance in this regard, until the 2% nC addition (Figure 2-B). The 4% and 5.5% nC2 addition was similar to the nC1 density measurements for these percentages of nMt. nC3 performed best, with densities equal to that of the reference paste for 0.5% and 1% nC3 addition (Figure 2-C). 2%, 4% and 5.5% nC3 performed similar to the former two.

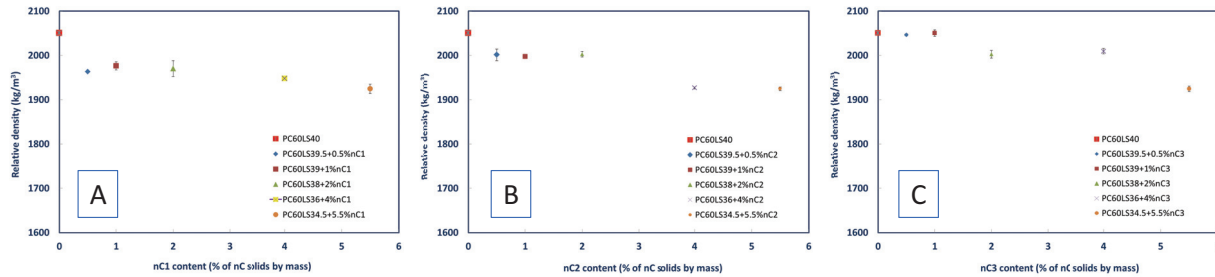


FIGURE 2. Long term relative density of (A) nC1, (B) nC2 and (C) nC3 added pastes.

With respect to the MIP measurements, nC1, which caused a significant reduction in density, also caused a significant increase in porosity and average pore diameter, in contrast to some other reported results suggesting that the organomodified nMt dispersions act as nanofillers, reducing the porosity [9] or the total pore volume [10] (Figure 3). In other words, as expected by the late age relative density results, nC1, was the only dispersion that caused an increase in porosity from day 1 to day 90. As also confirmed by the voids observed by SEM this could be the major reason for which the compressive strength of the nC1 modified pastes [6] was lower than that of the reference paste, certainly closely related to the chemistry and nanostructure of the organomodified nMt dispersion itself. In fact, the smaller average pore diameter was delivered by nC3 followed by nC2, possibly because of the better exfoliation and dispersion of the nMt platelets in the bulk of the aqueous dispersion. In effect, the inorganic nMt, being better exfoliated and dispersed at addition up to 1% offered similar density to the reference paste, and indeed triggered a reduction in porosity and average pore diameter size, in support of the argument that inorganic nMt can act as nucleation point and nanofiller.

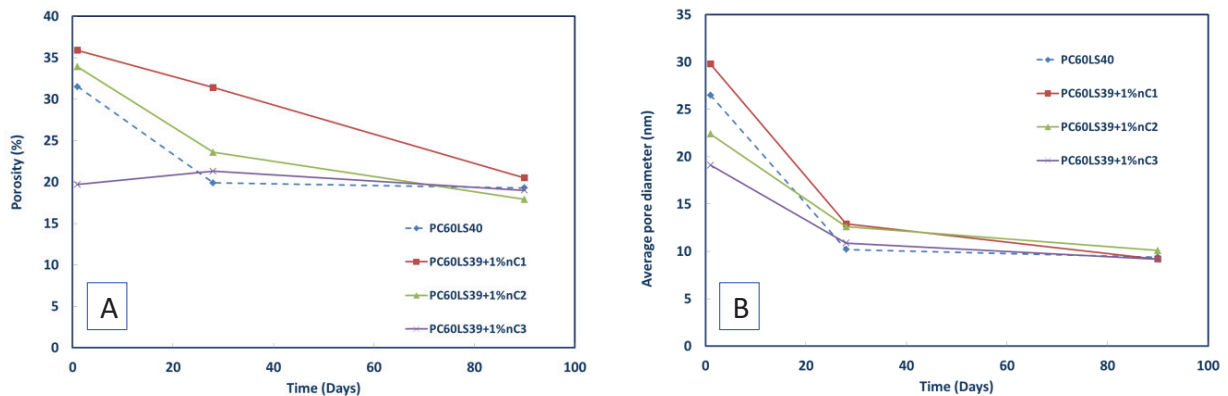


FIGURE 3. Effect of nMt dispersion type on (A) the porosity of cementitious nanocomposites and (B) the average pore diameter of cementitious nanocomposites.

CONCLUDING REMARKS

The results presented in this paper provided an insight into the effect the different nMt dispersions can have in cementitious nanocomposites with respect to microstructure, porosity and density, as investigated by different techniques which were eventually interrelated. The inorganic nMt dispersion, up until now overlooked by researchers, can, indeed, offer microstructural enhancement, which combined with other results already presented in the referenced papers can encourage further research in the use of inorganic nMt for tailored materials performance. In conclusion, the research presented herein pushed the envelope further by suggesting the use of inorganic nMt for superior material properties, while proved what type of surfactants should be avoided if organomodified nMt dispersions must be selected.

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