Nanotechnology offers an opportunity to modify and observe cement at the nanolevel. In this research, two aqueous suspensions of organomodified montmorillonite clay nanoparticles and one inorganic dispersion were added to blended cement formulations, consisting of Portland cement and limestone. The degree of dispersion of the modified montmorillonite nanoclay (nC) particles was verified by TEM. The role of the nC on the hydration of the cement pastes was verified by TG analyses of 1 to 170 days old, nanomodified cement formulations. Evidence of pozzolanic reactions promoted by the nC addition were only shown for the inorganic nC. Furthermore, compressive strength tests on the pastes placed an upper limit of 1 to 2% addition of nanoclay solids by mass of binder. FESEM images were also captured depicting the nanostructure of the modified formulations. Evidences suggest that the specific nanoclays can offer enhancement for flexural performance of blended cements with no degradation over time. The research reported was part of a much broader research project (FIBCEM) supported by the EU.
1 Introduction

Recent researches have demonstrated that using nanoparticles, has a significant effect on the chemical reactions taking place during cement hydration and on the structural characteristics of the hydrates, with subsequent effects at the macro level; that is to say, mechanical characteristics and durability of the hardened cement paste. The nanoparticles are more chemically reactive, since a greater surface area is available for reactions and/or they strengthen the nanostructure by minimizing the nanosized pores (0.5 to 5 nm wide) within the calcium silicate hydrates [1]. A whole new range of hybrid nanocements can be produced with the addition of a variety of nanoparticles, such as nano-SiO₂ [2-4], nano-montmorillonite clay [5], nano-Al₂O₃ [6], nano-TiO₂ [7]. In the current research nanoparticles of montmorillonite clay were used.

Montmorillonite is a naturally occurring, hydrophilic bentonite mineral, belonging to the smectite family of clays. It has been used in many industrial applications because it exhibits a high specific surface area, high surface reactivity and high cation exchange capacity. It is a three layer mineral in which an octahedral aluminium layer is sandwiched between two tetrahedral silicon oxide layers [5]. They can only be considered to comprise of individual nanoparticles ready for reactions if the bonds bridging the layers are weakened to the extent of separation of the layers. This happens when a modifier, is introduced within the galleries, causing a change in the charge of the molecules and a subsequent separation of the layers. If the modifier is organic, the clay is said to be organomodified, becoming hydrophobic. The clays used in this research, were Viscogel XDB bentonites, supplied by Laviosa Chimica Mineraria S.p.A. They were organomodified with methylbenzyl dihydrogenated tallow ammonium salts by Lietuvos Energetikos Institutas (LEI) and dispersed with the use of surfactants (steric stabilisers Zephrym or Synperonic 10/6) by the UK Materials Research Institute (MaTRI). As an effect, two different organomodified nanoclay (nC) dispersions were prepared; SnC and ZnC. In addition, the inorganic, unmodified sodium montmorillonite nanoclay, commercially available as Dellite HPS was also supplied by Laviosa Chimica Mineraria, dispersed with inorganic surfactant, by MaTRI, UK and used with the name InC in this research.

2 Experimental procedure

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.
- Limestone (LS) (additional), conforming to EN 197-1.
• Organomodified SnC and ZnC in an aqueous dispersion containing about 15% by mass of nC particles.
• Unmodified inorganic sodium montmorillonite nC, InC, in an aqueous dispersion containing about 15% by mass of nC particles.
• PVA fibers, kuralon H-1, 4 mm – only for samples tested in flexure.
• Superplasticizer visocrete 20HE – only for samples tested in flexure.

The nanoclays were characterized by Transmission Electron Microscopic (TEM) analyses (Fig.1). 10 μl of each nC dispersion was diluted in 100 ml of distilled water and small drops of the diluted solutions were dripped on copper mesh grids coated with a thin carbon film. Grids were dried at 25°C prior to the insertion in the instrument. Samples were examined at a voltage of 120 kV and micrographs were acquired with GATAN Jeol view camera.

Fig. 1: TEM micrographs of: A. SnC at 150000x, B. ZnC at 120000x, C. InC at 120000x

The SnC dispersion is depicted in Fig. 1A, showing significant local conglomeration. The SnC layers are covered with organic matter, possibly coming from the organic modifier and are stacking on top of each other. This arrangement does not allow the reactive sides to be exposed, hence no seeding effect can be expected and additionally can cause localized shear failures in the materials, and hence, cement pastes formulated with SnC were predicted to have lower compressive strengths. Fig. 1B shows ZnC, exhibiting areas of agglomeration, but at a more intercalated arrangement than SnC, expected, therefore, to perform better when mixed in cement pastes and verified with compressive strength tests. Fig. 1C shows InC, very well dispersed in which discrete platelets of nC can be identified, indicating that exfoliation has taken place, with some small agglomerates of impurities. Soft edges can be observed, lowering the possibilities of shear failure at the nanolevel.
2.2 Mix design
Fifteen ternary cement combinations were generated by using Portland cement, limestone, and either of the two organomodified nC dispersions or the inorganic nC dispersion. PC60LS40, a non-pozzolanic blended cement mix, containing only Portland limestone cement (PC) and additional limestone (LS), was used as the reference to investigate whether the addition of nC has a pozzolanic effect. nC 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 nC 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. Therefore, the general formula of the matrix of the ternary nanomodified cement pastes was:

\[ 60PC + (40 - x)LS + xnC \]  
(1)

Where \( x \) = % of nC solids at ranges from 0 to 5.5%.

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. The fresh paste was cast into cylindrical molds of 64 mm height and 32 mm diameter for compressive strength tests and samples of the pastes were also separately kept for compositional and microstructural analyses. Specimens were air cured in dry sealed conditions at 20±2ºC for the first 24 hours, then in water at 20±2 ºC, until the day of testing.

2.3 Analytical testing
A suite of compressive and flexural (three point bending) strength tests was carried out on at least three samples of each formulation at each age. To characterize the pastes, arrest of hydration was performed following two different methodologies as described by Calabria-Holley et al. [3]. Secondary electron imaging of the coated with chromium pastes was generated using a field emission electron microscope (FESEM) Jeol JSM 6301F. Thermogravimetric analysis (TGA) was carried out using Setaram TGA92. Each powder sample was placed in an alumina crucible and heated at a rate of 10°C/min from 20°C to 1000°C in nitrogen atmosphere.

3. Results and Discussion
A comparative study of the compressive strength on day 1, 7, 28, 56, 90 and 170 of pastes nanomodified with each of the three different nC dispersions was made. An overall decrease in compressive strength for the nC pastes can be observed when compared to the reference paste, PC60LS40, especially after day 28. This phenomenon can be explained as follows:
- Organomodified dispersions had low stability causing agglomeration of the nanoparticles, as observed by TEM analyses.
• Phase separation of ZnC was observed prior to mixing.
• ZnC and InC dispersions were very viscous and difficult to handle. Stirring the dispersion prior to mixing, may have not be enough to regain a homogeneous dispersion in turn agglomeration of the nanoparticles took place, inhibiting their potential for chemical reactions.

As can be observed in Fig. 2, improvements were achieved with 0.5-1% nC addition. Beyond this level no strength improvements were possible. Using these blended pastes as reference, three more fibre cement formulations were designed and specimens of 120x40x10 mm were created and tested in flexure containing: a) 60% PC, 40%LS, 3% PVA fibres and 2% superplasticizer (SP) by mass of binder (F.PC60LS40PVA3SP2), b) 60% PC, 39%LS, 3% PVA, 2% SP + 1%ZnC (F.PC60LS39PVA3SP2+1%ZnC) and c) 60% PC, 39%LS, 3% PVA, 2% SP + 1%InC (F.PC60LS39PVA3SP2+1%InC). It can be seen in Fig. 3 that flexural strength can be enhanced by the nanoclay additions by 10-30%, the results being more pronounced with InC, which additionally exhibited smaller variations in terms of standard deviation (smaller than 1 MPa) and an almost stabilized strength after 28 days.

![Fig. 2: Compressive strength of ZnC modified pastes](image)

![Fig. 3: Flexural strength of ZnC and InC modified pastes](image)
TG analyses were carried out showing some pozzolanic activity of the InC, with the consumption of approximately 10% of the Ca(OH)$_2$ present on day 28 in the reference paste - PC60LS40. However, the dispersing agents present in ZnC could account for the formation of extra Ca(OH)$_2$ crystals, a possible explanation for the lower compressive strengths.

Secondary image analyses showed a porous structure as a result of the addition of SnC (Fig. 4A) as well as with the addition of ZnC (Fig. 4B). However, the addition of InC (Fig. 4C) led to an apparently denser structure.

![Fig. 4: FESEM micrographs of PC60LS39+1%nC – day 28: A. PC60LS39+1%SnC at 5000x, B. PC60LS39+1%ZnC at 5000x, C. PC60LS39+1%InC at 5000x.](image)

### 4 Conclusions

The effect of the addition of three different dispersions of nC was investigated. The nanomodified blended cement pastes were particularly sensitive to the initial level of dispersion of the nC. Pozzolanic activity was more pronounced for the better dispersed nC particles, as shown by TEM analyses (Fig.1C). The inorganic nature of cement bore natural affinity with InC, which delivered better results than the organically modified nC. The addition of superplasticizers can improve the
consistence of the pastes, rendering the nC more effective. Improvements in flexural strength can be expected even at later ages, whereas enhancement of compressive strength is less probable if superplasticizers are not added.

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