Inorganic and organomodified nano-Montmorillonite dispersions for use as supplementary cementitious materials - A novel theory based on nanostructural studies

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Inorganic and organomodified nano-Montmorillonite dispersions for use as supplementary cementitious materials - A novel theory based on nanostructural studies

The compatibility of three nano-Montmorillonite (NMt) dispersions in hydrating cement binders was investigated and a new theory linking the nanostructure of nanoclay dispersions to their effect on the macroscale performance of cement pastes is presented. 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 characterized via TEM imaging and crystallography, XRD, SEM/EDX and TGA/DTG. With this characterization protocol, the way carbon loading and surfactants interact with the nanostructure of the nanoclay dispersions in light of their addition in composite cements was clarified. The suggested methodology is suited for the characterization of nanoclay dispersions and the entirely new theory developed will open up a new horizon for the understanding and exploitation of nano-Montmorillonite as a supplementary cementitious material.

Keywords: inorganic/organomodified nano-Montmorillonite dispersions; TEM imaging-crystallography; XRD; SEM/EDX; TGA/DTG; Si/Al

Introduction

In the past decade bentonite clay and its main phase, montmorillonite (Mt), a naturally abundant clay mineral, has gained momentum in concrete research as a supplementary cementitious material (SCM) 1-5. Mt, has a 2:1 layered structure and each layer consists of one alumino (Al–OH) octahedral sheet, held together between two siloxane (Si–O) tetrahedral sheets6. Mt layers have submicron lateral dimensions (100 nm to several microns) but their thickness is about 1 nm7. However, when used in its natural state as a
SCM, Mt has the disadvantage that water molecules are attracted and trapped between the layers and consequently it swells.

Various methods have been developed for the separation of these layers. This creates, so called, Nano-Montmorillonite (NMt), each particle of which is expected to be individually available for reactions. Furthermore, modification of the Mt at the nanoscale can hinder the swelling of the Mt nanoparticles in the hydrating cement environment. The separation of the Mt layers can be achieved using various chemical agents (dispersants, modifiers, surfactants) and depending on the application for which the nanocomposite is intended, the matrix in which the dispersion will take place (aqueous, polymeric, ceramic or metallic) is also selected. Three different states of the separation of the layers are identified in the literature (a) flocculation/face separation, (b) intercalation and (c) exfoliation. The second and the third type yield discrete NMt particles, whereas the first type is microsized. Furthermore, other arrangements are also acknowledged; face-to-face, edge-to-face and edge-to-edge.

The nature, nanostructure and production methods of Mt, with a focus on its use in cement and concrete pastes (complications, limitations and ways to mitigate these shortcomings) has been described in detail elsewhere. In summary, non-calcined NMt prepared for cement and concrete formulations, is dispersed in aqueous matrix with the help of chemical agents. If an organic modifier is used, an organomodified Mt nanocomposite is developed, principally by cation exchange, that is to say substitution of inorganic cations with cationic surfactants or modifiers such as alkylammonium salts. Recent research published on the effect of NMt in cement formulations, has been focused on the organomodified type. However, organomodification renders the Mt thermodynamically incompatible with the hydrating cement matrix. For this reason it has been suggested that if Mt is dispersed in water with a water soluble polymer, an
effective nanocomposite can be produced avoiding the organomodification process. Therefore, an inorganic dispersant, such as multivalent inorganic phosphates, can be used, which maintains the inorganic nature of Mt, while modifying the surface of the nanocomposite and impeding the edge-to-face configurations. Another option is anionic polyacrylates for steric stabilization. Using either of these inorganic surfactants; inorganic phosphates or polyacrylates, allows the Mt to preserve the hydrophilic nature of the NMt. In support of this, recent findings suggest that inorganic NMt may offer enhanced pozzolanic activation and revolutionary microstructural and strength improvement in cementitious composites.

Apart from the characterization of cement pastes enhanced with NMt, first and foremost, NMt must be characterized individually before being added to cement pastes. Research on NMt particles has been focused on the verification of the platelet separation achieved by the organomodification. Comparisons between X-ray diffraction (XRD) or wide angle X-ray diffraction (WAXD) analysis and transmission electron microscopy (TEM) imaging suggest that the interlayer space expansion of intercalated nanocomposites can be identified by WAXD or XRD, although in some cases basal reflections are not always well defined. However, when exfoliation has taken place the X-ray diffraction from the distributed silicate layers may disappear. On the other hand, TEM allows for the visual inspection of morphology, structural non-homogeneities and for other qualitative studies. Manias et al used TEM image analysis on 20-40 individual images to count the number of the various configuration of layers in the nanocomposite, postulating that XRD can only diffract orderly stacked layer, but for the observation of exfoliated layers TEM should be preferred. More recently, layer separation was witnessed via Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis/differential thermogravimetry (TGA/DTG) and
cation exchange capacity via chemical methods. Other studies on the organomodification of Mt based the confirmation of platelet separation on characterization via FTIR, TGA/DTG, XRD, TEM imaging and dispersibility measurements. It is interesting to note that Nie et al concluded that Sodium-Mt (Na-Mt) exhibited very good dispersibility in water. However, when dispersed in organic solvents Na-Mt agglomerated and sank at the base of the vial, in contrast to the organomodified Mt which showed greatest hydrophobicity. XRD and TGA have been used to study the changes in the NMt basal reflection with respect to the surfactant content. These studies were designed for the preparation of polymer nanocomposites or for environmental applications.

Limited research on the characterization of clay nanocomposites designed for use in cementitious composites has been carried out; and much less on the effect of NMt. Of the research published on the effect of the addition of clay nanocomposites in cementitious composites, results are restricted to the characterization of the nanomodified pastes or mortars rather than the clay nanocomposites themselves. Very few studies provide data on clay nanocomposites; for example, (i) Cloisite®30B organomodified Mt added to waste glass cement mortars was characterised by SEM imaging, (ii) organically modified smectite or (iii) organomodified Mt added to ordinary Portland cement was characterized by XRD and TEM imaging, (iv) organomodified Mt produced from purified Na-Mt with the help of quaternary ammonium salts was characterised by SEM, XRD, TGA and chemical analysis before added to type I cement mortars and (v) inorganic or organomodified NMt in aqueous suspensions for use in composite cement pastes has been examined via TEM imaging.

So far, only two scientific teams have described the optimization of organomodified Mt modification to be used in nanomodified cement pastes. In the first,
Cloisite® Na-Mt was organomodified with ammonium chloride. The exact amount of surfactant and the stability of the dispersion were determined via zeta potential and turbidity measurements, whereas the exfoliation of the sheets was verified via XRD. However, this research did not consider the possibility of modifying Mt while maintaining its inorganic nature. Furthermore, the separation of the layers could have been cross-checked with at least one more characterization technique. The second team recently presented a study on inorganic and organomodified Mt powders, initially characterised via TEM, XRD, SEM-EDX and TGA. Then, these NMt particles were dispersed in synthetic cement pore fluid simulating the alkaline cement environment. Suspension quality was determined via measurements of UV/vis and rheological studies over a range of surfactant concentrations. Moreover, characterization with AFM and FTIR at different pH environment exhibited the significant potentials of inorganic NMT for greater stability and increased C–S–H production in hydrating cement binders.

From the above it can be concluded that (a) a comprehensive methodology for the characterization of nanoclay dispersions with the scope for it to be used in cementitious composites is yet to be developed, (b) inorganic NMt has been neglected and a comparison between inorganic and organomodified NMt dispersion properties with regard to its use in cementitious composites is lacking, (c) the relationship between the nanostructure of the NMt and the macroscale effects resulting from their addition in cementitious composites is still undefined. In this paper, the above-mentioned issues have been addressed through the characterization study of three nanoclay dispersions. The paper presents a new theory relating the nanostructure of the NMt dispersion to the expected macroscale performance in NMt enhanced cementitious composites that sheds light into this field of cement science.
Materials and Methods

Materials

The present research was produced within the scope of a much broader research project in which the effect of various nanoparticles on the hydration, microstructure and strength of composite cements was examined. Two organomodified NMt dispersions and one inorganic NMt dispersion were used as described below.

Organomodified NMt dispersions (nC1 and nC2)
The nanoclay used for organomodification was a purified bentonite suspension (containing 3.9% of Mt, CEC 105 meq/100 g) produced by Laviosa Chimica Mineraria S.p.A. It was organomodified by exchange of basal metal cations with methylbenzyl di-hydrogenated tallow ammonium chloride (Noramonium MB2HT) by colleagues at Lietuvos Energetikos Institutas (LEI). Although other quaternary alkylammonium salts have been employed by other researchers for the organomodification of bentonite, benzylmethyl di-hydrogenated tallow ammonium chloride, (Noramonium MB2HT), has never been used so far as a Mt organomodifier, and hence no studies on the effect of the specific nanoclay in cementitious matrices have been published. Properties of Noramium MB2HT: active material 83.77 %, the average molecular weight 640 g/mol. Research to obtain the optimal salt dosage for the organomodification of the bentonite suspension, to characterize the original and modified properties and the processes involved were all carried out at LEI. The modifier to clay ratio employed was 1:1 by mass, producing Viscogel XDB powder, named as “XDB” hereafter. This organomodified Mt was used as the base for two organomodified dispersions.
Organomodification creates a hydrophobic nanocomposite, which is incompatible with water, causing extensive flocculation of particles, when dispersed. This fact was overcome with the use of surfactant technology. Dispersion of the nanoclay was carried out by using:

1. 5% by mass fatty alcohol and 1% by mass defoaming agent to create nC1, and
2. 5% by mass alkyl aryl sulphonate to create nC2.

The presence of defoaming agent in nC1 was expected to affect the foaming performance of the cement pastes in which nC1 would be added. With respect to nC2, the concentrated dispersion showed evidence of phase separation; however, very small clay particle size was achieved. The highest nanoclay loading achieved in water was 15%.

**Inorganic nano-montmorillonite dispersion**

The inorganic NMt powder used for the NMt dispersion is commercially available under the name Dellite®HPS. It is derived from the purification of bentonite by Laviosa Chimica Mineraria S.p.A. and exhibits a high cation exchange capacity (CEC = 128 meq/100g). This NMt will be referred to as “HPS” hereafter. HPS, is by nature compatible with water. However, the electrostatic interaction of particles does not allow high clay loading in aqueous solutions. For this reason, the introduction of inorganic dispersant was considered necessary. Sodium polyphosphate (STPP) was used for the dispersion of the inorganic NMt, HPS. The inorganic dispersion produced, was called nC3 in this research and again, the NMt loading achieved in the aqueous dispersion was 15%. The inorganic nC3 dispersion remained homogeneous at all times. Properties of the three nanoclay dispersions are given in Table 1.
Table 1: Summary of nanoclay dispersion properties

<table>
<thead>
<tr>
<th>Sequence of evolution of the NMt</th>
<th>Initial Mt powder</th>
<th>Initial d value (nm)</th>
<th>Modifier</th>
<th>Modified clay d value (nm)</th>
<th>Dispersant</th>
<th>Final nanosized dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>From modified bentonite to nC1</td>
<td>Purified Mt suspension</td>
<td>1.24</td>
<td>Noramonium MB2HT</td>
<td>3.55</td>
<td>fatty alcohol &amp; defoaming</td>
<td>Organomodified aqueous dispersion</td>
</tr>
<tr>
<td>From modified bentonite to nC2</td>
<td>Purified Mt suspension</td>
<td>1.24</td>
<td>Noramonium MB2HT</td>
<td>3.55</td>
<td>alkyl aryl sulphonate</td>
<td>Organomodified aqueous dispersion</td>
</tr>
<tr>
<td>From purified bentonite to nC3</td>
<td>Dellite® HPS Mt</td>
<td>1.22</td>
<td>n/a</td>
<td>n/a</td>
<td>sodium tripolyphosphate</td>
<td>Inorganic aqueous dispersion</td>
</tr>
</tbody>
</table>

Proposing a comprehensive and inclusive characterization methodology for these three NMt dispersions and forming a theory on the expected effect of their nanostructural characteristics on the macroscale performance in cement binders comprises the purpose of the current paper.

**Methods**

The three dispersions were characterized as received; the level of exfoliation and single crystal structure via TEM, the bulk crystallographic characteristics via XRD, the elemental composition via SEM/EDX and thermal characteristics via TGA/DTG, with a view to be added in cement formulations. For TEM analyses suspensions of the NMt dispersions were produced, whereas for XRD, TGA and SEM/EDX the three NMt dispersions were vacuum dried as analytically explained below.
Suspensions at 10ng/ml were prepared from the NMt with distilled water. Small drops of the diluted solutions were then deposited 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 with a GATAN Jeol JEM 1200 mkII. Images were recorded on a Gatan Dual View camera.

When a polycrystalline structure, with randomly oriented grains, forming rings is detected, having the camera constant known, the calculation of the lattice spacing is allowed according to the following adapted formula\textsuperscript{25}:

\[
\frac{r}{2L} = \frac{\lambda}{d} \rightarrow d = \frac{2\lambda L}{r}
\]  

(1)

Where L: the camera length and \( \lambda \): the electron wavelength, which are independent of the specimen and constant for the TEM instrument and \( d = d \)-value and \( r \) = distance from the diffraction centre. Since \( d \) is inversely proportional to \( r \), the largest \( d \) value is obtained by the innermost ring. For the specific TEM diffraction analysis, \( \lambda L = 1 \). These results can be compared with \( d \)-value measured by XRD. The only variable measured with the help of the TEM software was \( r \), manually taken to be equal to the distance between the centre of the diffraction and the centre of each individual ring. As an effect, greater error is expected when comparing TEM and XRD \( d \)-value measurements.

**X-ray diffraction (XRD)**

For XRD analyses the NMt dispersions were first vacuum dried for three days at a pressure of 10-2 mbar (100 Pa). The dried dispersion samples were then crushed to fine powder, passing the 125 μm sieve. XRD measurements were performed using a D8 ADVANCE X-ray diffractometer with CuKα radiation. Spectra were obtained in the
range $4^\circ < 2\theta < 20^\circ$ at an angular step-size of 0.016° $2\theta$. Analysis of reflections and d value were calculated according to Bragg’s law ($n\lambda = 2dsin\theta$) 26.

The state and extent of dispersion - exfoliation of the NMt can be examined by XRD and TEM analysis. Apart from mineralogical analysis, XRD is used to probe the structure and measure the interlayer spacing by monitoring the basal reflection of the silicate layers. Changes in basal spacing offer an indication of the intercalation of the NMt. TEM and in specific the study of diffraction patterns can clarify the extent of dispersion or exfoliation of the NMt. For example, if the NMt is polycrystalline a series of rings will be observed or if it is highly crystalline a spot pattern will emerge.

Scanning electron microscopy/ X-ray energy dispersive spectroscopy (SEM/EDX)

For SEM/EDX imaging and elemental composition analyses the NMt dispersions were first vacuum dried for three days at a pressure of 10-2 mbar (100 Pa). The dried dispersion samples were placed uncoated on a sheet of molybdenum, an element absent from the NMt dispersions for unbiased elemental analyses. A matrix of 5 x 5 spectra was acquired and the median of the elemental composition was presented. The Si/Al ratio was also calculated and the standard deviation shown. Samples were imaged using a Jeol 6480 LV SEM.

Thermogravimetric analyses (TGA)

For TGA the NMt dispersions were first vacuum dried for three days at a pressure of 10^{-2} mbar (100 Pa). The dried dispersion samples were vacuum dried and crushed to fine powder, passing the 125 μm sieve. Thermogravimetric analyses (TGA) were carried out using a Setaram TGA92 instrument. Approximately 20 mg of each sample were placed in an alumina crucible and heated at a rate of 10°C/min from 20°C to 1000°C 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.

**Results**

The three NMt dispersions exhibited significant physical (Figure 1-A, B and C) and chemical differences for their use in cementitious composites.

![Figure 1: Physical appearance of (A) nC1, (B) nC2 and (C) nC3 dispersions](image)

**TEM imaging and crystallography**

**Organomodified dispersion nC1**

The TEM micrograph (Figure 2) and the diffraction pattern (Figure 3) of nC1 indicate that it was possibly intercalated, but not exfoliated and particles tended to re-agglomerate locally. This could be attributed to the high clay loading in the dispersion (15% by mass). TEM imaging showed that the nC1 layers were covered with organic matter, possibly coming from the organomodifier or from the surfactant and were stacking on top of each other, in a combination of primarily face to face arrangement.
and edge to edge or face to edge arrangements. This arrangement does not allow the reactive sides to be exposed, hence limited seeding effect can be expected when used as an addition to cementitious composites. Additionally, this could initiate localized shear failures in the NMt composite, with cracks propagating between the stacks of layers (Figure 4 (A) and (B)). As a result, cement pastes formulated with nC1 were predicted to have lower compressive strengths due to poor bonding, and presence of significant amounts of impurities. Indeed, results already published verify poor compressive strength of composite cement pastes produced with the addition of nC1.

Acquiring diffraction patterns for nC1 proved to be an elaborate process due to re-agglomeration of the particles on drying. The diffraction pattern of nC1 (Figure 3) shows a polycrystalline structure, with randomly oriented grains, since rings are present. Two diffraction patterns were collected and the various d value values were calculated according to Equation (1). The values obtained for diffraction pattern B were: d1 = 2.85 nm; d2 = 1.64 nm; d3 = 1.09 nm; d4 = 0.96 nm and d5 = 0.79 nm.
Figure 2: TEM micrograph of nC1 (A) 6,000x (B) 10,000x, (C) 50,000x and (D) 120,000x
Figure 3: TEM diffraction patterns of nC1

Figure 4: A: Possible shear failure as a result of the arrangement of NMt platelets, B: possible nanocrack propagation path around limestone or unhydrated cement solids
**Organomodified dispersion nC2**

The TEM imaging analysis of nC2 confirmed the presence of smaller agglomerates as seen in Figure 5. The particles at greater magnifications seem to be intercalated and exfoliated, however, the presence of organic matter is still pronounced as in the nC1 imaging. Stacks of platelets are visible at magnifications greater than 25,000x with a combination of primarily face to face arrangement with edge to edge or face to edge arrangements. Again, this platelet exfoliation is not considered favourable for enhancing the compressive strength of cement formulations however, more discrete layers are visible and significantly less agglomeration seems to be taken place. This organomodified NMt dispersion is expected to perform better as strength enhancement in nanocomposite cements.

Several diffraction patterns were collected; two of which are shown in Figure 6. The various \(d\) value values were calculated according to Equation (1). The values obtained for diffraction pattern A were: \(d_1 = 2.86\) nm and \(d_2 = 1.59\) nm; \(d_3 = 1.05\) nm; \(d_4 = 0.92\) nm; \(d_5 = 0.8\) nm and \(d_6 = 0.76\) nm. The values obtained for diffraction pattern B were: \(d_1 = 2.85\) nm; \(d_2 = 1.64\) nm; \(d_3 = 1.02\) nm; \(d_4 = 0.90\) nm; \(d_5 = 0.79\) nm and \(d_6 = 0.76\) nm. Other diffraction patterns gave the same order \(d\) value values. This demonstrates the greater homogeneity and better dispersion of nC2, compared with nC1 as all single crystals examined showed an increased basal spacing.

It is interesting to note that the \(d\) values calculated from the diffraction patterns of nC2 were similar to those derived by single crystal analyses of nC1, since the same modifier was used for both NMt. However, for the better dispersed and less agglomerating nC2 the acquisition of diffraction patterns was significantly easier and the values obtained amongst the patterns were more consistent.
The TEM diffraction patterns of nC2 dispersion, showed a marginally greater number of rings, implying slightly more polycrystalline structures than nC1 and more randomly scattered crystals (white spots amongst rings). It is acknowledged that black and white prints of TEM diffraction patterns are subject to personal interpretation and for this, the raw image is presented. The lines of the rings in Figure 6 also appear to be on average less diffuse than those in Figure 3. It should be noted that the samples were tilted in order not to mistake excitation errors for white spots inferring scattered crystals.

Figure 5: TEM micrograph of nC2 (A) 10,000x (B) 25,000x, (C) 75,000x and (D) 120,000x
Inorganic dispersion nC3

Figure 7 shows nC3, very well dispersed in which discrete platelets of NMt smaller than 50 nm can be identified, indicating that although the d value is lower than in the organomodified NMt, exfoliation has taken place, with some small agglomerates of impurities. Disordered distribution of irregularly shaped layers can be observed. Soft, rather than angular edges are imaged, lowering the possibilities of shear failure at the nanolevel. nC3 overall looks the most stable of all three dispersions.

Two diffraction patterns (Figure 8 (A) and (B)) were collected, showing a great number of rings, i.e. many diffracting planes, more exfoliated crystals and greater homogeneity. The various d values were calculated according to Equation (1). The values obtained for diffraction pattern A were: d1 = 2.78 nm and d2 = 1.47 nm; d3 =
1.03 nm and d4 = 0.91 nm. The values obtained for diffraction pattern B were: d1 = 2.35 nm; d2 = 1.30 nm; d3 = 0.86 nm; d4 = 0.76 nm and d5 = 0.63 nm.

Figure 7: TEM micrograph of nC3 (A & B) 60,000x, (C) 75,000x and (D) 120,000x

Figure 8: TEM diffraction patterns of nC3
**X-ray diffraction (XRD)**

*Organomodified dispersion nC1*

The XRD analysis of nC1 (Figure 9) showed a marginal increase in the d value of the 001 plane (reflection at 2.2° 2θ). From 3.55 nm achieved by the modification as shown in Table 1, it was increased to 3.95 nm by the dispersion process. The reflection at 4.4° 2θ corresponds to the 002 plane, while the reflection at 6.6° 2θ corresponds to the 003 plane. Adding to this, it seems that the surfactant used for nC1 increased the d values. Higher order reflections such as (002 and 003) are typical of regular stacking of the modifier chains in the interlayer space.

Both diffraction patterns for nC1 dispersion delivered similar d values, however lower than the values obtained by XRD. The reason for this is that XRD is measuring the d value in the bulk of the material, whereas TEM is focused on a single crystal. On the other hand, the difference reported could also be attributed to the sample orientation during TEM measurements, since the length of the platelets is several nm. Apart from the fact that the particles seem to be re-agglomerating on drying, most importantly, the intercalated platelets, being periodically stacked are traceable by the XRD, whereas the exfoliated platelets being fully disordered remain XRD silent. For this reason, it is herein suggested that both methods are employed when characterizing the d value of a nanoclay composite.

*Organomodified dispersion nC2*

XRD analysis of nC2 dispersion showed a d value of 3.95 nm at 2.2° 2θ and 2.0 nm at 4.4° 2θ (Figure 9). Comparing the d value derived from the XRD analyses of the modified NMt powder (XDB) and of the modified and dispersed nC2, it can be assumed that nC2 platelets remained dispersed in the solution, i.e. comprised of discrete
nanoparticles within the dispersion having the same d value at approximately the same 2θ angles, since it was the modification that caused the lattice expansion. Adding to this, it seems that the surfactant used for nC2 increased the d value by 0.1 nm.

Taking the argument further, it is known that d value corresponding to the XRD reflections is used as a means of measuring the degree of exfoliation. However, as exfoliation takes place, there should also be a broader spread of different d value values present, hence multiple XRD reflections may appear due to the fact that some layers may be easier to intercalate/exfoliate in the presence of the modifier, whereas others may be more resistant. Reflections and may also be wider if not XRD silent. Two approaches could be followed to assess this hypothesis. Either measuring the full-width at half maximum of the reflections or carrying out base line correction and mathematical curve fitting and comparing the full widths. The second technique was adopted, as the WIRE software available could provide exact and mathematically elaborated values. Comparing curve 1 in Figure 9 and Table 2, it can be observed that nC1 exhibited a smaller width value, while nC2 a greater width value compared with the starting NMt powder, XDB.

Furthermore, the higher counts that nC1 exhibits can be attributed to the diffraction of the re-agglomerating particles due to the different surfactant used and also non-intercalated platelets present, as observed by TEM. In fact, other researchers also report increasing peak intensity with aggregated particles of NMt in a polymer matrix, caused in their case, by increasing doping level of NMt which consequently inhibited intercalation. Most commonly, though, ordered arrays of NMt platelets form monolayer, bilayer, trilayer or paraffin-type layer arrangements, traceable by XRD and identifiable according to the basal spacing measured. On the contrary, nC2 and the starting NMt powder XDB bear greater similarity in terms of peak intensity. Still,
exfoliated, disordered and homogeneously distributed layers, present no periodic stacking and for this, they remain XRD silent, a condition that is more valid for the inorganic NMt. nC1 and nC2 dispersions, as well as the starting XDB powder exhibit distinct peaks implying the presence of ordered (non-exfoliated or re-agglomerating) stacks of platelets.

Table 2: Width and height of XRD reflections of nC1, nC2 as compared to starting NMt powder XDB

<table>
<thead>
<tr>
<th>XDB</th>
<th>Centre</th>
<th>Width</th>
<th>Height</th>
<th>nC2</th>
<th>Centre</th>
<th>Width</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>2.23</td>
<td>0.42</td>
<td>7002.93</td>
<td>Curve 1</td>
<td>2.21</td>
<td>0.61</td>
<td>4352.50</td>
</tr>
<tr>
<td>Curve 2</td>
<td>4.38</td>
<td>0.57</td>
<td>3200.33</td>
<td>Curve 2</td>
<td>4.35</td>
<td>0.71</td>
<td>1440.63</td>
</tr>
<tr>
<td>Curve 3</td>
<td>6.55</td>
<td>0.65</td>
<td>1120.55</td>
<td>Curve 3</td>
<td>6.44</td>
<td>0.81</td>
<td>778.15</td>
</tr>
<tr>
<td>Curve 4</td>
<td>8.75</td>
<td>0.70</td>
<td>299.84</td>
<td>Curve 4</td>
<td>8.55</td>
<td>0.85</td>
<td>200.87</td>
</tr>
</tbody>
</table>

nC1

<table>
<thead>
<tr>
<th>Centre</th>
<th>Width</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>2.49</td>
<td>0.55</td>
</tr>
<tr>
<td>Curve 2</td>
<td>4.66</td>
<td>0.90</td>
</tr>
<tr>
<td>Curve 3</td>
<td>7.07</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 9: XRD reflection shifts of nC1 & nC2 with addition of surfactants as compared to starting XDB
Inorganic dispersion nC3

XRD analysis of nC3 dispersion was also carried out (Figure 10), showing a d value of 1.49 nm (higher than the non-expanded HPS) at 5.9° 2θ and 0.45 nm at 19.7° 2θ shifted reflections as expected for unmodified Mt. Most importantly, the typical Mt reflection at 19.7° 2θ was marginally traceable, as is the case for exfoliated, disordered Mt layers.

As discussed in the case of nC1, nC2 and XDB with regards to the comparative XRD analyses, the reflection shift and difference in width between nC3 and the starting NMt, HPS is also presented. As shown in Figure 10 and Table 3 the width of the first reflection was almost equal in both samples, whereas the reflection of nC3 was shifted towards lower 2θ angle.

Comparing the d values derived from the XRD and TEM analyses it can be assumed that nC3 remained dispersed in the solution, i.e. comprised of discrete nanoparticles within the dispersion.

A level of disparity between TEM and XRD d values is always expected, as discussed earlier. Additionally, the overall lower d values given by the TEM diffraction analyses could be attributed to the material preparation method; vacuum drying of samples may have caused some imbalance to the nature of the specimens.

Table 3: Width and height of XRD reflections of nC3 as compared to original HPS

<table>
<thead>
<tr>
<th>nC3</th>
<th>Centre</th>
<th>Width</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>5.98</td>
<td>1.18</td>
<td>900.41</td>
</tr>
<tr>
<td>Curve 2</td>
<td>19.76</td>
<td>0.24</td>
<td>76.18</td>
</tr>
<tr>
<td>HPS</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Curve 1</td>
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</table>


**Elemental analysis**

**Organomodified dispersion nC1**

SEM/EDX analysis was performed so that the elemental composition would be determined. For high statistical reliability of the elemental analysis a matrix of 5 x 5 randomly selected spectra was collected. Indicatively the first five are presented in Table A1 in the appendix. For nC1 the Si/Al ratio was found to be between 4.02 and 4.48 with a median of 4.23 and a standard deviation of 0.12, significantly higher than the ratio obtained for the modified only NMt. The carbon content was found to be significantly high (44-55% atomic). Knowing that the amount of organic modifier added to the NMt was equal to 41% by mass, the difference could be attributed to the presence of the organic surfactant. The high carbon content could possibly lead to formation of carboaluminates when nC1 would be added to the cement paste. A
comparison of the elemental composition of all NMt dispersions and the starting NMt powders in terms of the median of the atomic percentage normalized by 100% is provided in Figure 11. Lastly, the comparison of the Si/Al ratios of the three NMt dispersions is given in Figure 12.

Organomodified dispersion nC2

The EDX analysis showed that nC2 contained almost the same amount of carbon as nC1 (about 47-59% normalized atomic) for the same reasons stated above, as indicatively shown in the first five spectra in Appendix, in Table A2. The Si/Al ratio was similar to nC1 (Figure 12) and was found to be between 3.86 and 4.39 with a median of 4.08 and a standard deviation of 0.14. Figure 5-A and -B show areas of agglomeration in the nC2 dispersion and areas of crystallization of impurities, but at a more intercalated arrangement than nC1. Consequently, it can be expected to perform better when added to cement pastes. However, it is interesting to note that the elemental analysis of nC1 did not show any Na, implying that all Na cations were exchanged as intended during the NMt modification. EDX elemental X-ray diffraction analysis on nC2 showed traces of Na in various spectra and this is because for nC2 an anionic surfactant containing Na, was used, also shown in Figure 11.

It can be postulated, by further observation of the elemental compositions of the three NMt dispersions (Figure 11), that the dispersing procedure of the starting NMt was partially successful for the two organic dispersions. As a matter of fact, nC1 and nC2 dispersions were composed of less C and more Si and Al than the initial organomodified NMt, XDB. However, the over 50% atomic normalized percentage of carbon in nC1 and nC2, is expected to contribute to significantly different performances at the macroscale. This observation can be coupled with the TEM image analyses,
showing layers covered with organic matter for nC1 and nC2, possibly not allowing the individual platelets to perform as a nucleation sites for hydration reactions.

**Inorganic dispersion nC3**

EDX elemental analysis showed low carbon content; between 7.8 and 9.0% normalized atomic. The Si/Al ratio was found to be between 2.60 and 3.97 with a median of 2.71 and a standard deviation of 0.08, therefore close to the theoretically expected value for Mt of 2.60 and hence, lower than nC1 and nC2 (Figure 12). The Ca content ranged from 0.7 to almost 2.0%. When used in a cementitious composite Ca could potentially take part in the C–S–H forming hydration reactions or acting as a seeding agent 31.

The comparison of the elemental composition acquired by the SEM/EDX between nC3 and HPS, from which the former was developed, showed that both the original clay and the dispersed NMt contain only small quantities of C, compared to nC1 and nC2 and significant quantities of Si, Al and O (Figure 11). Apparently, the dispersant increased the carbon content. What is of interest is that the atomic normalized percentage of carbon content in the inorganic dispersion reached approximately 9%, compared to over 50% traced in nC1 and nC2 (Figure 11). However, the quantities of Si and Al were twice higher than those measured in nC1 and nC2 dispersions, expected, therefore, to contribute to significantly different performances at the macroscale.
The comparison of the Si/Al ratios of the three dispersions provided further evidence of the variation observed in the organomodified dispersions since the standard deviation of these samples was higher than that of the inorganic dispersion (Figure 12).

In hydrating cement pastes $C-S-H$, the main hydration product is nanosized and its chemical, structural and physical characteristics affect the performance and durability of cement and concrete$^{31,32}$. Given that lower Ca/Si ratio corresponds to denser $C-S-H$ gel network$^{33}$ and knowing the Si and Al content and the Si/Al ratio of NMt, cement scientists can manipulate the characteristics of the $C-S-H$ formed in NMt enhanced cementitious composites. Although the standard deviation of the observed Si/Al ratio for nC1 and nC2 seems to be marginally higher than that of nC3, it could be argued that such variations would only be insignificant for applications at the macroscale. The extremely high surface area available with the use of NMt dispersions and the seeding
effect that NMt particles exhibit when added to cement formulations may be significantly affected by such differences at the nanolevel. Further research on NMt enhanced cementitious composites is required for confirmation of this hypothesis.

Figure 12: Comparison of the Si/Al ratios of nC1, nC2 and nC3 dispersions

**Thermal gravimetry**

The dispersions were analysed via TGA/DTG in order to assess any changes within the structure, after the addition of the surfactants. For comparison TGA/DTG data of the inorganic nanoclay (HPS) and organomodified nanoclay (XDB) prior to dispersion are also given. The mass loss peaks are shown in Figure 13 and Figure 14. Apart from loss of free water, four regions of mass loss of organomodified Mt powders are identified in literature (i) up to 200°C associated with adsorbed interlayer water, (ii) from 200°C to 500°C associated with the decomposition of organic elements (modifiers and surfactants) attached to the Mt platelets usually exhibiting two peaks due to different structural arrangements and (iii) between 550°C and 800°C associated with the loss of structural water from the Mt, known as dihydroxylation.
The modifier of the organomodified dispersions was designed to be entirely decomposed by 500°C. TG/DTG/DSC carried out on the modifier by Lukošiūtė & Čėsnienė has revealed five endothermic peaks:

- At 41°C melting of materials commences
- At 105°C evaporation of solvents takes place
- At 185°C, 321°C and 414°C deconstruction of the modifier is completed
- By 450°C, 88.9% of the total material was decomposed

As an effect the mass loss at these temperatures is partly assigned to the aforementioned reactions related to the organomodifier.

Moreover, comparing the results of the XDB powder and the organomodified and dispersed nC1 and nC2 (Figure 13 and Table 4) the first peak at 70°C and the second peak at approximately 200°C of XDB occurred at the same temperature for nC1 and nC2. The third peak occurred at 330°C with a shoulder at 400°C for XDB, whereas for nC1 it was shifted by 30°C and for nC2 the peak was shifted by 80°C. These three distinct regions can be assigned to the following mass losses; (i) below 200°C it is associated with adsorbed interlayer water, therefore almost the same amount of water is adsorbed by both dispersed NMt, (ii) at around 200°C the decomposition of the modifier took place and can be observed in Figure 13 similar amounts are present for nC1 and nC2, (iii) at approximately 350°C the modifier molecules physically adsorbed on the surface of the Mt layers are lost and (iv) at around 420°C the modifier molecules inserted in the interlayer space through cation exchange are bound to the surface of the layers via electrostatic interaction are decomposed.

The dTG curves of nC1, n2 and XDB are similar below 300°C, however between 300°C and 500°C differ substantially. The peaks and shoulders presented for nC1 are shifted compared to the peak and shoulder of the XDB within this temperature
range, whereas for nC2 this shift is even more pronounced. This suggests that the surfactant used in nC2 provoked different structural arrangements of its molecules in the interlayer space \(^{27}\) which resulted in better affiliation of the surfactant in the dispersion. In a way, this result was expected given that the alkyl aryl sulphonate is anionic, therefore, causes charge interaction as opposed to the surfactant used in nC1 which was non-ionic. It is possible that in the complex chemistry of the organomodified and dispersed NMt the anionic surfactants contribute to the formation of stronger bonds, in agreement with other researchers who used an ion-exchange bromide as surfactant and modifier \(^{36}\). For further analysis of such results, ionic strength measurements can be performed, which, however remain beyond the scope of the current research \(^{37}\).

The quantitative analysis of the differential mass losses of nC1 and nC2 at the different temperature ranges, yielded a number of interesting observations:

Upon closer examination, most of nC1 decomposed within the 280-400°C temperature range, whereas for the decomposition of nC2 greater energy was required. Although the organomodification was designed in such a way that the decomposition of the modifier bound to the bentonite occurred at 380-500°C (XDB curve showing mass loss of 21.3% with a peak at 400°C) the surfactant used in nC1 possibly produced a dispersion which is easier to thermally decompose at lower temperatures; whereas the surfactant used in nC2 produced a more thermally durable dispersion, enhancing the structure of XDB. Above 500°C marginal mass loss assigned to the dihydroxylation of the bentonite was traced in both NMt dispersions. Therefore, the peak shifts of nC1 and nC2 dispersions compared to the starting XDB powder NMt do not correspond to errors, but rather represent different enthalpy of the nanocomposite \(^{35}\).
Figure 13: dTG curves of nC1 and nC2, compared to the starting XDB NMt powder

Table 4: Decomposition peaks of NMt dispersions and starting NMt powders

<table>
<thead>
<tr>
<th>XDB</th>
<th>nC1</th>
<th>nC2</th>
<th>nC3</th>
<th>HPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°C</td>
<td>70°C</td>
<td>70°C</td>
<td>85°C &amp; shoulder at 110°C</td>
<td>68°C</td>
</tr>
<tr>
<td>200°C</td>
<td>198°C</td>
<td>213°C &amp; shoulder at 360°C</td>
<td>656°C</td>
<td>685°C</td>
</tr>
<tr>
<td>330°C &amp; shoulder at 400°C</td>
<td>360°C &amp; shoulder at 411°C</td>
<td>410°C</td>
<td>750°C &amp; shoulder at 830°C</td>
<td>-</td>
</tr>
</tbody>
</table>

Lastly, the dispersed inorganic nC3 (Figure 14 and Table 4) showed a typical decomposition behaviour with three primary mass losses. The first significant one occurred at around 85°C with a right shoulder at 110°C and was attributed to the loss of the adsorbed interlayer water. This loss was much greater than that of HPS, the original unhydrated powder NMt, as expected, since according to literature clays adsorb water if directly dispersed in aqueous solutions. Furthermore, two other mass losses were recorded for nC3; one small peak at 650°C and a more pronounced one at 750°C with a right shoulder at 830°C attributed to the loss of structural water – dihydroxylation of the
Mt$^{38,39}$. The last peak can be attributed to the decomposition of the tripolyphosphate surfactant which typically takes place at 600°C.

![dTG curve of nC3 compared to the starting HPS NMt powder](image)

Figure 14: dTG curve of nC3 compared to the starting HPS NMt powder

**Discussion**

Overall, the level of intercalation or exfoliation of the NMt layers/platelets will affect the mechanical properties of the cement pastes into which the NMt dispersions will be added. In fact, research on ternary NMt enhanced pastes containing Portland cement (PC, 60% by mass), limestone (LS, 39.5% by mass) and NMt dispersion (solid content of 0.5% by mass), showed relatively poor performance of the NMt dispersions in terms of cylinder compressive strength of pastes, whereas much better performance in terms of flexural strength$^4$ as shown in Figure 15 and in Figure 16. In greater detail, nC2 showed the best performance compared to the other organomodified dispersion, nC1, while nC3 outperformed reference paste and nC2 in flexure$^4$. 
Figure 15: Cylinder compressive strength of NMt enhanced Portland limestone cement pastes adapted from literature \(^5\) (Reference mix 60% Portland cement, 40% limestone; NMt replaced limestone by 0.5% solid content).

Figure 16: Flexural strength of NMt enhanced Portland limestone fibre cement pastes adapted from literature \(^5\) (Reference mix 60% Portland cement, 40% limestone; NMt replaced limestone by 0.5% solid content – also included PVA fibres and superplasticizer (SP) at 3% and 2% by mass of total solid content respectively).
Three different configurations can be suggested for the analysed NMt dispersions. In the first case (Figure 17 (a)) the sheets were not exfoliated and therefore will possibly remain agglomerated in the volume of the cement paste. The re-agglomeration of layers brought nC1 back to the micron size, hence reduced the variability in the sizes of the particles, within the paste (Figure 18 (a)). As an effect, larger voids are to be expected and cracks could propagate amongst the bigger elements. Although the d value between the platelets was similar for nC1 and nC2, the different surfactants changed the structure of the NMt platelets, which could be more prone to splitting apart. This weakness, could in turn attract nanocrack propagation between the platelets, rendering nC1 enhanced pastes more brittle and less resistant in either tension or compression.

![Diagram showing configurations of NMt dispersions](image)

Figure 17: Effect of platelet condition within the cement paste- (a) non-exfoliated layers, (b) exfoliated and dispersed layers and (c) some layers exfoliated/some intercalated
Figure 18: Effect of NMt exfoliation level on particle size distribution in cement paste – (a) more brittle configuration around re-agglomerated platelets and (b) less brittle to ductile configuration

The nanostructure of nC3 dispersion is depicted in Figure 17 (b). As the exfoliated layers/platelets were dispersed in the volume of the paste they may act as nanoreinforcement. The particle size distribution is therefore enhanced, while the NMt platelets may also be acting as nanofillers (Figure 18 (b)). This configuration also allows for the benefits of increased specific surface area of the platelets to be delivered. At the same time, individual platelets can bend freely within the paste and can therefore introduce an obstacle to the crack propagation (tortuous crack pattern propagation). Such platelet arrangements favour less brittle behaviours, hence the addition of nC3 is expected to deliver more ductile cementitious composites, favouring flexural strength development but with no compressive strength enhancement.

In the third case (Figure 17 (c)) some layers were exfoliated and some remained intercalated in the volume of the dispersion. This case is more representative of nC2, the major difference with nC1 being that some layers are better dispersed. The anionic
surfactant used in nC2 differentiated the mechanical performance of the nC2 enhanced pastes significantly. In fact, the higher energy bonds do not allow the slippage of the NMt platelets, which, then, act as nanoreinforcement stopping the propagation of nanocracks through the NMt (tortuous crack pattern propagation). This condition can lead to more ductile behaviour and increases in flexural strength. However, the fact that some platelets are not exfoliated or tend to agglomerate, may induce areas of weakness when nC2 dispersion is added to cement pastes.

Results presented on the effect of the three different nanoclay dispersions in compressive strength of cement formulations and flexural strength of fibre cements verify these hypotheses and pave the way for further investigations on the use of nanoclays in advanced low carbon footprint cements.

Conclusions

Different techniques for modifying and dispersing NMt or NMt affect the nanostructure, the thermal properties and elemental composition of the final NMt dispersion in different ways. NMt dispersions are so sensitive that even in cases in which the same NMt is used as a starting material but the surfactant changes, variable properties can be engineered. For this reason, thorough characterization is required to gain more understanding on how the NMt dispersions perform and how they are structured before they are used in cementitious composites. This is the first study presented on the characterization of NMt and NMt dispersions in light of their use as SCM. Organomodified NMt and inorganic NMt dispersions were investigated and it can be concluded that:

- NMt powders and NMt dispersions must be adequately characterized before being implemented in cement pastes and their level of dispersion must be
determined. In fact, XRD, TEM diffraction analysis, TEM imaging, EDX elemental analysis and TGA combine a suitable and adequate methodology.

- The level of exfoliation should be verified by single crystal analysis, although it is acknowledged that many diffraction patterns must be collected and analysed.
- Elemental composition analysis can provide an insight of the C–S–H formation potentials of the various nanoclays.
- Knowing the NMt and surfactant decomposition stages is essential before carrying out TG analysis of NMt enhanced cement pastes.
- Anionic surfactants are more suitable for dispersing NMt for use in cement combinations. Non-ionic surfactants produce less stable dispersions in which the layers tend to re-agglomerate as verified by TEM imaging and XRD.
- Inorganic NMt dispersions can deliver more promising results towards the production of sustainable cements.
- The nanostructure of the NMt dispersions greatly affects their stability and, therefore, their expected performance in the hydrating cement environment. A theory linking these two elements is presented.

Acknowledgements

The authors acknowledge the European Commission funding (FIBCEM project, grant Number 262954) and all partners are thanked for their input and for the supply of materials. Dr Irena Lukošiūtė and Dr Jūratė Čėsnienė from LEI, Lithuania, are thanked for providing significant clarifications. The authors would also like to acknowledge the Department of Chemical Engineering at the University of Bath for the use of the TGA. Dr Thomas Dyer, University of Dundee, is thanked for scientific discussions and Dr Manuel Nuño for his assistance with XRD experiments.
## Appendix

### Table A1: SEM/EDX counts summary (% atomic) of nC1

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<thead>
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<th>Spectrum</th>
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<th>Mg</th>
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<th>P</th>
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<th>Cl</th>
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<tr>
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### Table A2: SEM/EDX counts summary (% atomic) of nC2

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### Table A3: SEM/EDX counts summary (% atomic) of nC3

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References


32. Papatzani S, Paine K, Calabria-Holley J. The effect of the addition of


