

# **Influence of the organically modified nanoclay on properties of cement paste**

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## **ABSTRACT**

The effect of the organically modified nanoclay on the properties of cement paste was investigated. The cement pastes used in this study were a mix of water with ordinary Portland cement and organoclay at water-to-solid ratios (w/s) 0.27, 0.31 and 0.36. Three organically modified clays were used for replacement: two are commercially available and one was produced in laboratory. Cement was partially replaced for three organoclays with the dosage of 0.5%, 1%, 2%, 4% and 6 % by the weight of cement. Samples were tested after 7 and 28 days of hydration. DSC/DTG/TG and XRD analysis of organoclay as well as modified cement paste was performed. The results revealed that depending on w/s ratio and the type of organoclay used samples with cement substitution for organoclay showed from 2 % up to 14 % higher compressive strength results than that of the plain cement paste. It was also observed that with increasing w/s ratio higher amount of cement can be replaced by organoclay. After 28 days of hydration, regardless which one of organoclay was used, lower water absorption than that of the plain cement paste was established only for the samples at w/s=0.27.

Key words: nanoclay, cement, modification, strength, DSC/DTG/TG, XRD

## **1. INTRODUCTION**

Portland cement is one of the most widely used construction materials in the world. However, the production of Portland cement leads to the release of a significant amount of

CO<sub>2</sub> so called greenhouse gas. Environmental issues are playing an important role in the sustainable development of the cement and concrete industry.

Nano-montmorillonite (bentonite) is the most common member of smectite clay family usually referred as “nanoclay”. Nanoclay consists of layer made of an inner octahedral sheet of alumina or magnesia sandwiched between two tetrahedral sheets of silica. Addition of nanosized layered silicates into the Portland cement systems accelerates the cement hydration and application of nanoclay as reinforcement of cement and concrete is promising in enhancing the mechanical performance as well as reducing permeability and shrinkage of the concrete <sup>[1-5]</sup>. The results of microstructural analysis indicate that the nanoclay behaves not only as a filler that improves microstructure, but also as an activator that promotes pozzolanic reaction in modified cement matrix <sup>[6]</sup>. Due to the better interaction of nanoclay particles with cement minerals there it is important to distribute homogeneously these layered particles in the nanoclay-cement composites pastes. In most cases this is achieved by organic cation exchange modification of clay where the organic compound is inserted into the interlayer space of the clay minerals as a cationic species or a neutral molecule under certain conditions <sup>[1,2,7]</sup>. Nanoclays are less expensive than other nanomaterials, because the basic materials come from readily available natural sources and because they are produced in existing, full-scale production facilities <sup>[7]</sup>. Organoclays produced by treatment of clay minerals such as bentonite and montmorillonite with organics have a lot of applications in many fields of industry due to their specific active sites and attractive adsorptive properties <sup>[2,7-9]</sup>. On the other hand, the study of Nano-montmorillonite clay modification by using different types of alkylammonium salts indicated that surface modification has impact on interlayer space between the silicate layers as well as on cation exchange capacity of the clay <sup>[10]</sup>.

However, there is a lack of information about the influence of organically modified nanoclays on the properties of cement and consequently this is the main objective of this experimental study. Three nanoclays modified with different alkylammonium salts were chosen for this research. The influence of partial replacement of Portland cement by organoclay and water content on the compressive strength as well as on the water absorption of the cement matrix was investigated.

## 2. EXPERIMENTAL

### 2.1 Materials

Ordinary Portland cement type CEM II/A-L 42.5 N (PC) supplied by enterprise Akmenes Cementas Lithuania was used in this study. Chemical composition and physical properties of cement are given in Table 1. Three types of modified nanoclays were used for production of various cement pastes compositions at water-to-solid ratio (w/s) 0.27, 0.31 and 0.36. Commercially available modified nanoclay Dellite<sup>®</sup> 43B (denoted as 43B) and Dellite<sup>®</sup> 67G (denoted as 67G) were supplied by Laviosa Chimica Mineraria, Italy. The physical and chemical properties of organoclay are listed in Table 2. The third modified organoclay was produced in the laboratory and denoted as LM. Bentonite nanoclay Delite LVF (CEC 105 meq/100g) and quaternary ammonium salt ( $M \sim 610$  g/mol) was used as raw materials for production of organically modified nanoclay LM. In order to substitute all interlayer ions by  $\text{NH}_4^+$ , the required amount of modifier was calculated according to bentonite CEC.

Measured specific surface area  $S_{\text{BET}}$  of as produced organoclay was  $6.4 - 6.9$  m<sup>2</sup>/g and average pore size –  $2.19 \cdot 10^2$  Å. Measured average particle size of modified LM nanoclay was 7-10 µm.

Table 1 Chemical composition and physical properties of PC (provided by Akmenes Cementas)

Compound	Mass %	Physical property	Values
SiO <sub>2</sub>	20.61		
Al <sub>2</sub> O <sub>3</sub>	5.45		
Fe <sub>2</sub> O <sub>3</sub>	3.36	Particle size, µm	5-30
CaO	63.42	Specific gravity, g/cm <sup>3</sup>	2.75-3.20
MgO	3.84	pH value	11-13.5
SO <sub>3</sub>	0.80		
Others	2.18		

Table 2 Physical and chemical properties of Dellite<sup>®</sup> 43B and Dellite<sup>®</sup> 67G (provided by Laviosa Chimica Mineraria)

Property	Dellite <sup>®</sup> 43B	Dellite <sup>®</sup> 67G
Moisture, %	3	3
Impurities content, %	<1	<1
Density, g/cm <sup>3</sup>	1.6	1.7
Particle size, μm	7-9	7-9
Modifier	Dimethyl benzylhydrogenated ammonium tallow	Dimethyl dihydrogenated tallow ammonium

In cement paste compositions cement was partially replaced by each organoclay with the dosage of 0.5 %, 1 %, 2 %, 4 % and 6 % by weight of cement. Organoclay was mixed with water and then was incorporated into the cement matrix following the procedure described in [2,7]. Plain cement paste was molded as a reference material. The wet cement pastes were poured into steel moulds after complete mixing. The specimens were demoulded after 24 h. Samples were kept at (20 ± 2) °C temperature and (95-100) % relative humidity until each curing age (7 and 28 days) was achieved.

## 2.2 Methods

A particle size distribution analysis of modified clays was carried out on a CILAS<sup>®</sup>1090 particle size analyzer with pressure of 7000 mbar at dry state.

X-ray analysis was carried out on Bruker Discovery diffractometer with CuK<sub>α</sub> radiation at 35 kV and 20 mA. Scanning was carried out from 1 ° up to 70 ° 2θ at 0.01 ° intervals. Interlayer space of the samples was calculated according Bragg's law. The hydration products were identified by commercial Search Match program.

Microstructure analysis was carried out on ZEISS EVO MA10 scanning electron microscope on the samples coated with gold in secondary electron mode and operated at 20 kV.

Thermogravimetric analysis was carried out on a Linseis STA PT1600 analyzer. Approximately 15-17 mg of powdered samples were continuously heated in a flowing nitrogen atmosphere at a heating rate of 10 °C/min from 25 °C up to 1000 °C temperature.

As the reference material for DSC/TG results analysis plain cement samples after 28 day hydration mixed with pure  $\text{Al}_2\text{O}_3$  powder (4 %) was used.

The Zwick Roell universal test machine of the capacity up to 50 kN and equipped with the testExpert<sup>®</sup> program was used for the compression test. Compressive strength test was performed at the rate of 0.5 mm/min according to LST EN 196-1 on the samples after 7 and 28 days of hydration. Results were expressed as average value of 10 measurements.

Bulk density, water absorption and volume of permeable voids results were obtained following the Archimedes method using water as the immersion liquid in accordance with ASTM C642 and literature <sup>[11,12]</sup>. Water absorption test was carried out on the specimens after 28 days of hydration. Three samples of each composition were dried in a convection oven at  $(100 \pm 5)^\circ\text{C}$  until the constant weight was reached and the dry mass of each sample was recorded. Dry specimens were totally immersed in water and then boiled for 5 hours. After 24 hours' time-exposure in water at  $20^\circ\text{C}$ , constant mass of the sample suspended in water as well as saturated surface-dry mass were recorded. Bulk density and water absorption were calculated from these data.

### 3. RESULTS AND DISCUSSION

Comparison of the particle size distribution of all three modified organoclays was performed and is presented in Fig. 1. It shows that particles of organoclay produced in laboratory (LM) distribute in the same range as commercial clays Dellite<sup>®</sup> 43B and Dellite<sup>®</sup> 67G. Moreover, approximately 60 % of volume is composed of particles with diameter up to 10  $\mu\text{m}$  in all clays used. Thereby the particles of three types of investigated organoclays are in the same size range as ordinary Portland cement's particles.

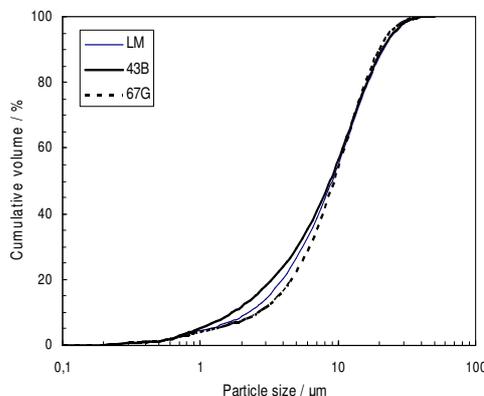


Fig. 1 Particle size distribution of modified clays

Micrographs of bentonite nanoclay before and after organic modification are presented in Fig. 2. Particle of bentonite has a closely knit surface while the surface of the modified clay particle is extended and lamellas are unclosed. Broader X-ray diffraction peaks of clays (Fig. 3) show broad distribution of interlayer spacing values due to disordered arrangement of molecules or ions of modifier in interlayer space. Initial d-spacing of clays were calculated according to Bragg's law from XRD patterns and they were 1.8 nm, 3.6 nm and 3.56 nm for 43B, 67G and LM, respectively. As can be seen from Fig. 3, the XRD peak of laboratory produced modified clay (LM) is shifted towards higher  $2\theta$  values and has a slightly lower interlayer spacing than 67G, but higher than 43B. Comparison of Thermo gravimetric analysis of modified organoclays shows that the main mass loss take place in the temperature range from 248 °C up to 436 °C and depends on the type of modifier used as well as on the interaction of modifier with bentonite (Fig. 4). The maximum of DTG peaks correspond to decomposition of the modifier situated in the interlayer of the each organoclay which is in accordance with [2].

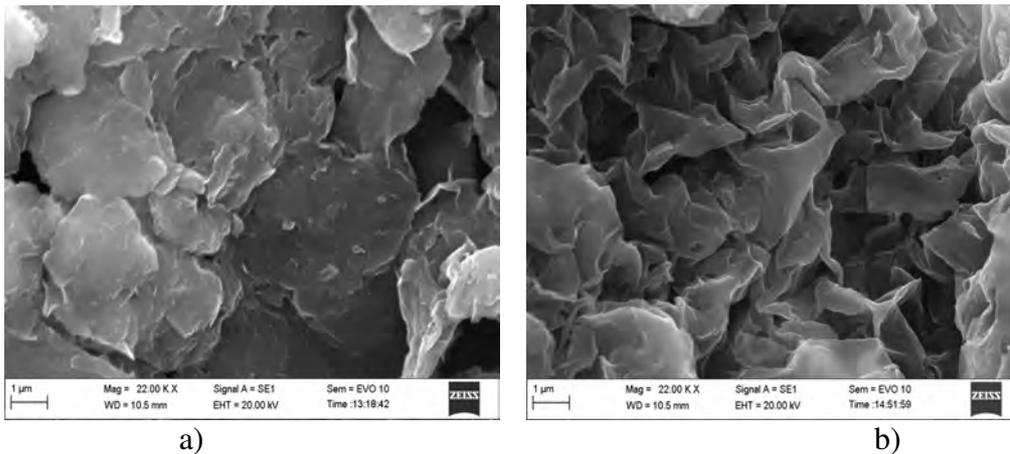


Fig. 2 Nanoclay before (a) and after modification (LM) (b)

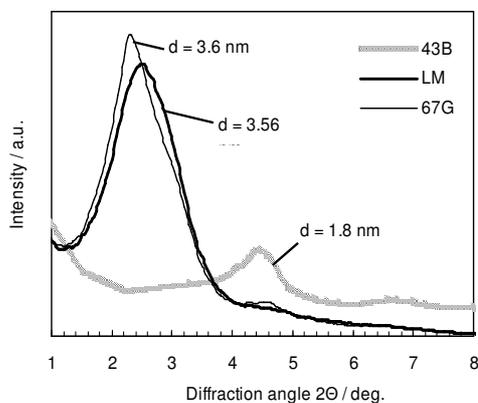


Fig. 3 XRD patterns of organoclays

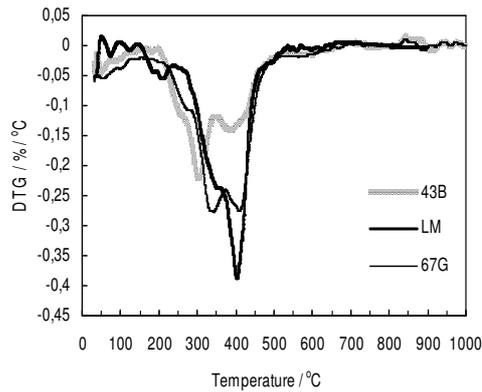


Fig. 4 DTG profiles of organoclays

The average compressive strength results of cement substituted with three organoclays at various dosages and w/s ratios are presented in Fig. 5-7. Distribution of compressive strength results shows that after 7 days of hydration at w/s = 0.27 (Fig. 5 a) even a low dosage of cement substitution for the organoclay has impact on the strength of the sample. Replacement of cement with 0.5 % and 1.0 % of the nanoclay 43B gives an increment in strength up to 8 % with afterward reduction from 3 % up to 27 %. In the case of nanoclay 67G increment in strength up to 2 % was achieved only at dosage of 1.0 %, while at higher dosages only the reduction of strength was identified. However, the lowest strength results were found for the samples with LM addition. After 28 days of hydration (Fig. 5 b) strength increments or the same strength as the plain cement paste were observed for all samples up to 2 % of cement substitution for all organoclay used. The maximum increment in strength up to 2 %, 7 % and 14 % was achieved with organoclay 67G, LM and 43B respectively (Fig. 5 b). Higher content of organoclay in the paste tends to reduction of strength (Fig. 5 b). The strength increment at low dosages of nanoclay was also observed at w/s = 0.31 after 7 and 28 days of hydration (Fig. 6). Cement substitution with clay 43B and 67G gave an increment in strength from 5 % up to 12 % at the clay dosages from 0.5 % to 1.0 % after 7 days (Fig. 6 a). Compressive strength up to 4 % higher was determined only for samples with 1 % of organoclay LM addition (Fig. 6 a). Approximately the same compressive strength as in the case of the plain cement paste was achieved when cement was substituted for 2 % and 4 % of organoclays 43B and 67G respectively (Fig. 6 a). Contrary, at the same dosage the drop in strength from 8 % up to 13 % was found for organoclay LM (Fig. 6 a). However, substitution of cement for 6 % of organoclay diminishes compressive strength up to 20 % at w/s = 0.31 after 7 days of hydration.

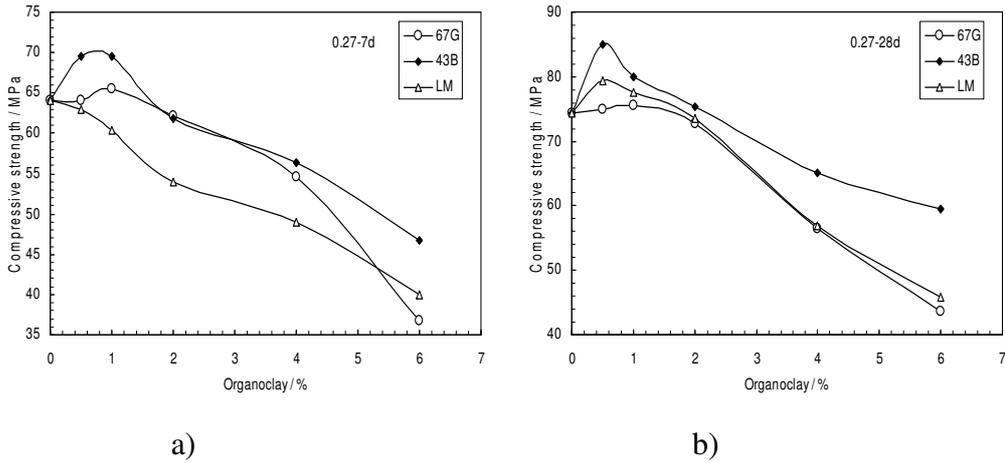


Fig. 5 Compressive strength of cement pastes as a function of organoclay content after 7 (a) and 28 (b) days of hydration at  $w/s = 0.27$

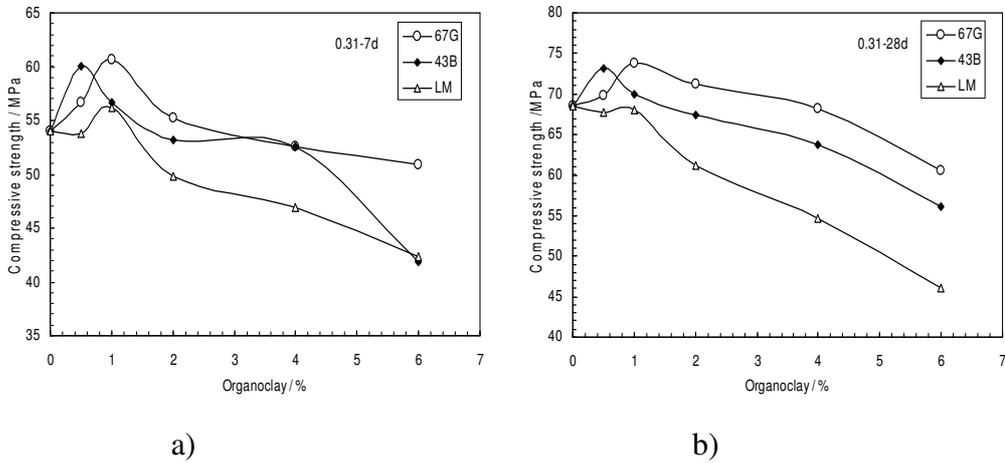


Fig. 6 Compressive strength of cement pastes as a function of organoclay content after 7 (a) and 28 (b) days of hydration at  $w/s = 0.31$

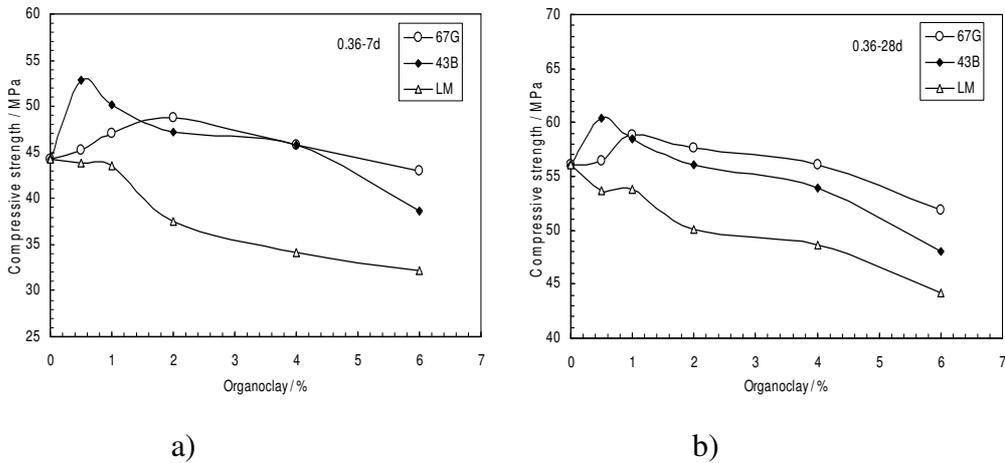


Fig. 7 Compressive strength of cement pastes as a function of organoclay content after 7 (a) and 28 (b) days of hydration at  $w/s = 0.36$

Longer hydration period allows replacing up to 4 % of cement by nanoclay 67G and to sustaining the same or up to 8 % higher compressive strength than the plain cement paste (Fig. 6 b). Contrary, lower amount of cement (1 ~2 %) can be replaced without the drop in strength when organoclay 43B or LM is used (Fig. 6 b). At dosages range from 0.5 % up to 1 % the maximum increment in strength was 7 % for 43B, while samples with organoclay LM showed almost the same strength as the plain cement (Fig. 6 b).

When w/s ratio increased up to 0.36, the compressive strength of samples modified with organoclay 43B and 67G was higher than of the plain cement paste after 7 days of hydration (Fig. 7 a), and the maximum increment up to 8 % and 5 % was measured for 43B and 67G respectively. Results also show that it is possible to replace even 6 % of cement by organoclay 67G without any reduction in strength (in the case of 43B, up to 4 %), while organoclay LM can replace only 1 % of cement (Fig. 7 a). Moreover, organoclay LM used for cement replacement showed the lowest strength results at all dosages after 28 days (Fig. 7 b), meanwhile the maximum rise in strength up to 5 % and 8 % was measured for 67G (at 1 %) and 43B (at 0.5 %) respectively. It was also observed that at dosages higher than 2 % the drop in strength is more gradual for all organoclay used at w/s = 0.36.

Analysis of the results obtained after 28 days of hydration (Fig. 5 b-7 b) shows that due to various modifiers used for nanoclay modification the compressive strength results strongly depend on the type of organoclay and water content used in the system. The higher is w/s ratio the higher amount of cement can be replaced by organoclay when the same or even higher compressive strength than the plain cement can be achieved. Results revealed that organoclay 43B can replace up to 2 % of cement at all w/s ratios tested, while LM can replace the same amount of cement only at w/s = 0.27. Organoclay 67G can replace up to 4 % of cement, but water content in the system should be 0.31 or higher.

The relationship between compressive strength (after 28 days of hydration) and bulk density as a function of w/s ratio is presented in Fig. 8. It indicates that the higher is the density, the higher is compressive strength of samples; however, density decreases with the increasing of w/s ratio. Despite the fact that three different organoclays were used, the density of the samples was very similar. For example, the average density of samples with 43B, 67G and LM reduces from 1.86 up to 1.70 g/cm<sup>3</sup>, from 1.83 up to 1.69 g/cm<sup>3</sup> and from 1.81 up to 1.66 g/cm<sup>3</sup> at w/s = 0.27 and at w/s = 0.36 respectively. Regardless of which of the organoclay was used, the variation in density was less than 3 % at the fixed w/s ratio, while at different w/s ratios density varied less than 9 %. According to <sup>[3,5]</sup>

reduction in density reflects higher amount of closed pores presented in paste with organoclay. It could be assumed that not all water is consumed in reactions with the cement during the mixing or hydration period, and there still is a part of water which is enclosed in the microstructure and produces open and closed porosity.

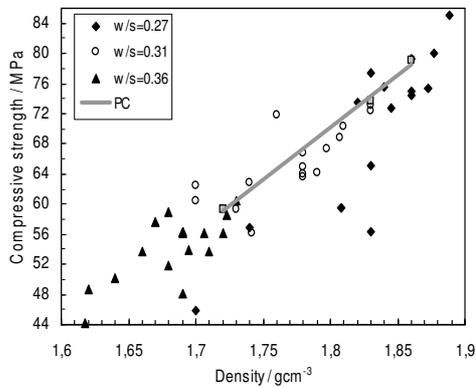


Fig. 8. Correlation between compressive strength and density as a function of w/s ratio. Hydration time is 28 days

Correlation between the volume of permeable voids and water absorption results are presented in Fig. 9, where volume of permeable voids of modified paste is lower than that of the plain cement paste only at w/s = 0.27. Volume of permeable voids increases with the increasing w/s ratio as well as the dosage of organoclay. It was observed that pastes modified with organoclays mostly at all dosages showed water absorption up to 10 % lower than that of the plain cement at w/s ratio 0.27. Additional water content in the paste tends to increment of water absorption in the sample due to a more open structure is formed.

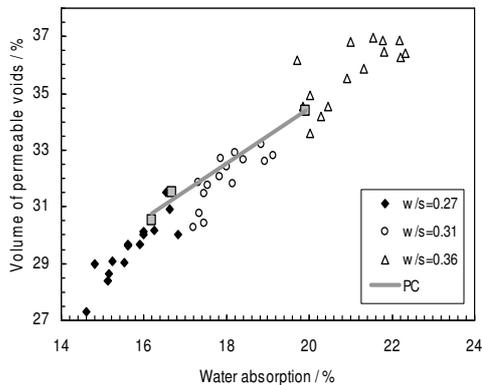
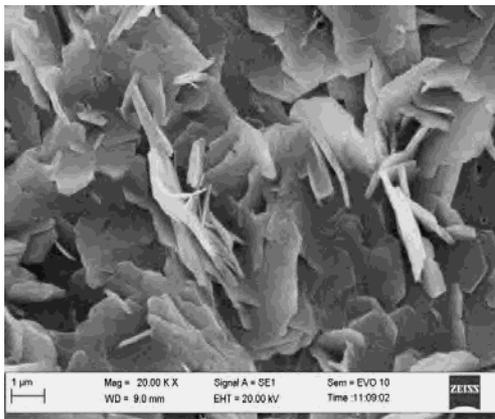
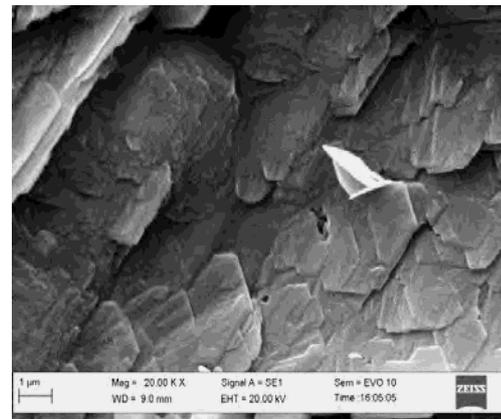


Fig. 9 Correlation between permeable voids' volume and water absorption as a function of w/s ratio. Hydration time is 28 days

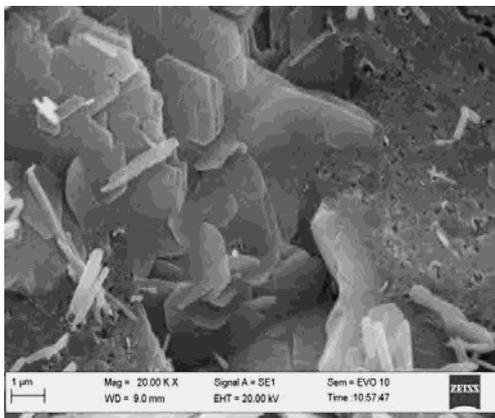
SEM images of unmodified and modified cement pastes are presented in Fig. 10. Addition of organoclay were found to influence the manner of hydration and resulted in differences in the microstructure of hardened cement compositions (Fig. 10). Typical plain cement microstructure after 28 days of hydration is presented in Fig. 10 a. When part of cement was replaced for organoclay, the hydrated products changed their structure (Fig. 10 (b, c)) and consequently, affected the strength of the pastes. SEM micrographs show that the higher amount of organoclay in cement composition the greater the differences in the hardened paste, that was confirmed by DSC/TG and XRD results.



a



b



c

Fig. 10 SEM micrographs of the cement compositions at  $w/s = 0.27$  after 28 days of hydration: plain cement (a); cement with 1 % of LM organoclay (b); cement with 4 % of LM organoclay (c)

Typical DSC/TG profiles of the plain cement as well as cement paste with modified organoclay hydrated for 28 days are presented in Fig. 11. The first endothermic peak (up to  $160\text{ }^{\circ}\text{C}$ ) in DSC profiles is attributed to the de-hydroxylation of the calcium silicate hydrate denoted as CSH phase and reflects evaporation of water from the layered structure of CSH

or other hydrates. The area of endothermic peak on DSC curve of the plain cement paste is very similar to the peak area of the paste with organoclay (4 %). Simultaneously, the weight loss on TG curve corresponds to 5.29 % and 5.35 % for plain and modified cement paste respectively (Fig. 11). In temperature range (160÷400) °C DSC curve of organoclay-modified cement paste shows more peaks, unlike the plain cement paste does, due to the de-hydration of calcium alumina and calcium alumina silica ferrite hydrates<sup>[13]</sup> as well as the decomposition of nanoclay modifier. These decompositions corresponds ~ 1 % of weight loss on TG curves (Fig. 11).

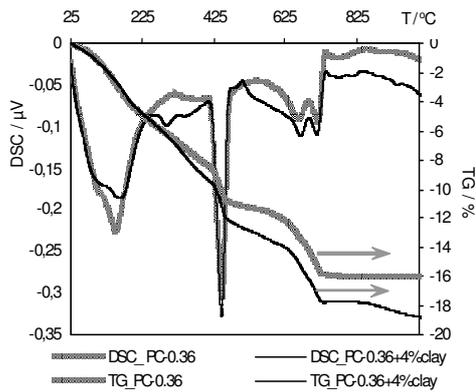


Fig. 11 DSC/TG profiles of plain cement and with organoclay addition

The major endothermic peak at ~ 445 °C corresponds to the de-hydration of calcium hydroxide denoted as CH. The areas of CH peak on DSC curve for the plain cement paste and the organoclay modified paste are alike. Consequently, the weight loss on TG curves is very similar – 2.93 % and 2.98 % for the plain cement and the modified one, respectively. The last double peak on DSC profile (~ 700 °C) is attributed to the decarbonation of calcium carbonate.

According to <sup>[14]</sup> higher total weight loss of the composition with organoclay (Fig. 11) can be attributed to the formation of other phases such as CASH or CAH during the conversion reactions of calcium hydroxide.

Also XRD analysis was done. Due to CSH gel is amorphous in nature it has no sharp and narrow peaks and thus is hardly detectible in XRD patterns. Typical XRD curves (at  $31^\circ < 2\theta > 36^\circ$ ) of samples hydrated for 28 days are presented in Fig.12. It was observed that portlandite (CH) peak is less intensive for the cement with organoclay than for the plain cement paste as well as the peaks of alite ( $C_3S$ ) and belite ( $C_2S$ ) (they overlap in Fig. 12). The higher the w/s ratio is, the more intensive the CH peak is, and the less intensive calcium silicates peaks in modified cement pastes (Fig. 12). This indicates that

the higher amount of water facilitates the cement hydration. It is known <sup>[5]</sup> that clay minerals act as nucleation agents for CSH hydration products and according to DSC and XRD results it is obvious that cement substitution with organoclay has impact on CSH formation inside the cement matrix, as well as on the compressive strength of the paste.

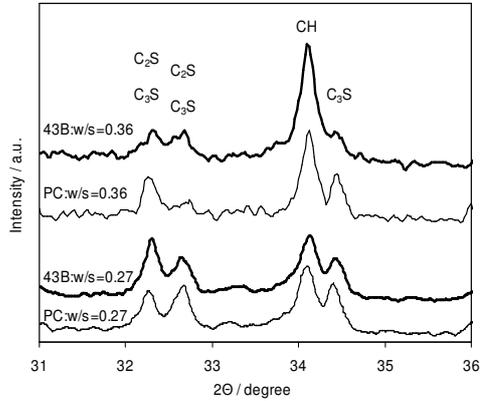


Fig. 12 XRD patterns of plain cement and with organoclay addition at various w/s ratios

## CONCLUSIONS

The impact of three organically modified nanoclays on the properties of cement pastes was investigated. Based on the experimental results the following conclusions can be drawn:

- Compressive strength of composite cement pastes strongly depends on the type of organoclays due to various modifiers applied for nanoclay modification and water content used in the system. The higher the w/s ratio is, the higher the amount of cement can be replaced by organoclay to achieve the same or even higher compressive strength than that of the plain cement. Samples with cement substitution by organoclay showed from 2 % up to 14 % higher compressive strength results, with strong dependence on w/s ratio. Up to 2 % of cement can be replaced by organoclay Dellite<sup>®</sup> 43B without reduction in strength at various w/s ratios; meanwhile, the maximum amount of organoclay LM used for cement replacement was 2 %, and that reduced with the increasing w/s ratio. Organoclay Dellite<sup>®</sup> 67G can substitute from 2 % up to 4 % of cement, when larger amount can be used at higher w/s ratios.
- Cement substitution by organoclay reduced water absorption of the paste up to 10 % at w/s=0.27. In the case of higher w/s ratio, water absorption increased regardless of which organoclay was used.

The reported experimental data show that under certain conditions it is possible to replace cement with organically modified clay and to obtain the same or better properties as that of the plain cement paste. Since the substitution of cement by organoclay has shown improvement in some studied properties, a further research is needed to develop its final prospective potential.

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