

## Influence of SiO<sub>2</sub>, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the properties of fly ash blended cement mortars<sup>2</sup>

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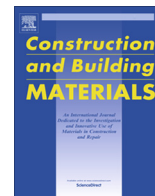
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## Influence of SiO<sub>2</sub>, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the properties of fly ash blended cement mortars

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### HIGHLIGHTS

- The influence of SiO<sub>2</sub>, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the properties of fly ash blended cement mortars has been investigated.
- Small amounts of nanoparticles have limited influence on the workability.
- Small amounts of nanoparticles result in higher compressive and tensile strength.
- Higher concentrations of nanoparticles have a negative impact on the strength.
- Addition of nanoparticles results in a reduction of open porosity of cement paste.
- Addition of nanoparticles modifies the micromechanical properties of cement paste.

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### ABSTRACT

This study explores the effects of different types of nanoparticles, namely nano-SiO<sub>2</sub> (NS), nano-TiO<sub>2</sub> (NT), and nano-Fe<sub>2</sub>O<sub>3</sub> (NF) on the fresh properties, mechanical properties, and microstructure of cement mortar containing fly ash as a supplementary cementitious material. These nanoparticles existed in powder form and were incorporated into the mortar at the dosages of 1%, 3%, and 5% wt.% of cement. Also, fly ash has been added into in mortars with a constant dosage of 30% wt.% of cement. Compressive and flexural strength tests were performed to evaluate the mechanical properties of the mortar specimens with different nanoparticles at three curing ages, 7, 14, and 28 days. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) tests were conducted to study the microstructure and the hydration products of the mortars. To elucidate the effects of nanoparticles on the binder phase, additional experiments were performed on accompanying cement pastes: nanoindentation and open porosity measurements. The study shows that, if added in appropriate amounts, all nanoparticles investigated can result in significantly improved mechanical properties compared to the reference materials. However, exceeding of the optimal concentration results in clustering of the nanoparticles and reduces the mechanical properties of the composites, which is accompanied with increasing the porosity. This study provides guidelines for further improvement of concretes with blended cements through use of nanoparticles.

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### 1. Introduction

Cementitious materials such as concrete and mortar are widely used in the construction sector. However, the environmental

impact of cement is not negligible. Every manufactured ton of cement contributes to the average emission of 0.7 ton of carbon dioxide to the atmosphere [1]. To mitigate this effect, research has focused on the use of more environmentally friendly binder alternatives, such as industrial by-products, to partially replace cement as a binder in concrete [2,3]. Mineral additives like fly ash, blast furnace slag, and silica fume have been widely incorporated into cementitious composites as supplementary

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cementitious materials (SCM's) for their economic and environmental advantages as well as their capability to reduce the micro and macro porosity of concrete [4]. However, the use of SCM's is also known to negatively affect some properties of concrete. For example, the pozzolanic reaction of fly ash is relatively slow. It only increases in speed after at least 7 days of hydration [5], therefore affecting the rapid development of engineering properties of concrete such as strength and stiffness. Feng et al. [6] reported that, in the first 3 days, the main contribution of fly ash to the strength of concrete is by the micro-aggregate and physical filling effect. The pozzolanic reaction of fly ash significantly increases the compressive strength of mortar after 60 days and the flexural strength after 28 days. However, the delayed setting and slow early strength development (up to 28 days) often restrict the utilisation of fly ash in practice since strength at 28 days of curing is commonly specified as the governing parameter for concrete in construction [7]. The lower strength at early age of 20% fly ash mixed concrete was reported to be a result wider microcracks present in the interfacial transition zone (ITZ). However, in mature concrete, this crack reduce in width, resulting in higher strength [8,9]. In general, the addition of fly ash in mortar can alter the microstructure greatly depending on its physical and chemical properties. Typically, using fly ash with finer particle size and higher calcium content of fly ash (Class F fly ash has low calcium content than Class C fly ash) results in lower porosity [10]. Lower porosity was reported in the interfacial transition zone (ITZ) area of carbonated fly ash based mortar when compared with uncarbonated fly ash mortar [10]. Studies have also shown that this porosity may be further reduced when 0.5% amorphous  $\text{SiO}_2$  nanospheres and  $\text{TiO}_2$  nanoparticles are added to the mix [11,12].

A nanoparticle is an elementary building block in nanotechnology and consists of up to thousands of atoms merged into a cluster of 1–100 nm. Such small size correspond with a high surface-area-to-volume ratio which enables them to have high reactivity as their behaviour is mostly affected by chemical reactions at the interface [13]. The use of nanoparticles has been expanding exponentially in various industries over the past decades. In the field of cementitious composites, the use of nanoparticles has been receiving increasing attention in recent years [14–16]. This is owing to the fact that nanoparticles have the potential to modify and improve the properties of the cement-based composite at a nano-micro structural level.

Different nanoparticles have been reported to enhance the early age strength of cementitious materials, and promote the pozzolanic reactivity of fly ash [14,17–19]. In addition, nanoparticles are expected to affect the kinetics and hydration reactions of cement significantly and generate a better effect in the filling of pores compared to other mineral additives, thus, enhancing the mechanical properties of mortar due to their large specific surface area and great electrostatic force [14]. However, the use of nanoparticles in cementitious materials does come with certain drawbacks: their large specific surface area and their tendency to agglomerate due to their strong inter-particle attraction (i.e., van der Waals forces) result in high water consumption. As a result, less free dispersant water is available for hydration [20]. Therefore, the incorporation of nanoparticles in cementitious composites can significantly alter the fresh and hardened properties of cementitious materials [21].

Most research has focused on the effects of nanoparticle addition on cementitious composites without the addition of mineral additives like fly ash [22]. A limited number of studies tried to determine the optimal amount of nanoparticles to enhance the properties of cementitious materials with the use of fly ash, and there is no consensus in the literature. For example, Mohseni et al. [18] reported that nano- $\text{SiO}_2$  (NS), and nano- $\text{TiO}_2$  (NT) have an optimum dosage of 3% and 5% per weight of cement replace-

ment, respectively. On the other hand, Oltulu and Sahin [14] reported that the optimum dosage for NS is 1.25% per weight of cement replacement. Similarly, for nano- $\text{Fe}_2\text{O}_3$  (NF), Oltulu and Sahin [14] have found the optimum dosage to be 1.25% whereas Yazdi et al. [23] have found it to be 3%, both per weight of cement replacement. In addition, influence of different types of nanoparticles in rheological, mechanical, durability, microstructural and thermal properties of concrete were investigated in several studies [24–27]. In most cases, it was concluded that the physical and chemical nature of nanoparticles may improve the concrete properties in noticeable level when compared with the concrete without nanoparticles.

Therefore, the focus of this research was to study the effect of different dosages of nano-silica, nano-titanium, and nano- $\text{Fe}_2\text{O}_3$  on the fresh properties, mechanical properties (i.e. compressive and flexural strength) and microstructure of mortars prepared with Ordinary Portland Cement (OPC) blended with fly ash. Cubic and prismatic mortar specimens were fabricated and tested to determine the mechanical properties of mortar. In addition, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) have been conducted to find out the link between hydration kinetics enhancement by the nanoparticles and the mechanical strength of the hardened mortars. To that end, also the porosity accessible to water has been measured and nanoindentation tests have been performed. The presented research will significantly contribute to the development of cementitious compo-sites containing OPC, fly ash and nanoparticles.

## 2. Experimental work

### 2.1. Materials

The binders used in this research were ordinary Portland cement (OPC), Class F fly ash and nanoparticles. Three different types of oxide nano-powders: nano-silica, nano-titanium, and nano- $\text{Fe}_2\text{O}_3$  were incorporated in the mortar mixtures. The physical properties of these nanoparticles have been shown in Table 1. Natural sand with a maximum grain size of 2 mm and a specific gravity of 2.66 was used as fine aggregate for the mortar. The specific gravity of OPC and fly ash was 3.1 and 2.2, respectively.

### 2.2. Mortar

#### 2.2.1. Mix design and mixing procedure

A total of 10 mixes with different proportions of binders (i.e. cement, fly ash and nanoparticles), aggregates and water were produced as tabulated in Table 2. For each proportion, specimens were tested at 3 curing ages: 7, 14 and 28 days. Cement was replaced by 30% of weight with fly ash in all mixtures. A constant water-to-binder ratio (w/b) of 0.485 and sand to binder ratio of 2.0 were used throughout the experiments. After preliminary testing of fresh and hardened properties performed with 5 different proportions of nano-silica (ranging from 0 to 10 wt% with 2% intervals), ratios corresponding to 1%, 3% and 5% by weight of cement replacement have been selected for all the nanoparticles incorporated into the mortar mixtures.

Nanoparticles tend to agglomerate due to their strong interparticle forces. Hence, nanoparticles were first mechanically mixed with water to produce a nanoparticle suspension and then mixed with the cementitious materials to achieve a more homogenous paste [18]. After casting, all specimens were kept in the moulds for one day at an ambient temperature of  $23 \pm 2$  °C and relative humidity  $65 \pm 5$  % and then demoulded and kept in a water tank for curing until testing.

**Table 1**  
Physical properties of nanoparticles (US-nano.com 2019).

Nanoparticle	Average diameter (nm)	Specific Surface Area (m <sup>2</sup> /g)	Purity (%)	True density (g/cm <sup>3</sup> )
Nano SiO <sub>2</sub>	20–30	180–600	99.5	2.40
Nano Fe <sub>2</sub> O <sub>3</sub>	20–40	40–60	99.0	5.24
Nano TiO <sub>2</sub>	15	60	99.5	3.90

**Table 2**  
Material compositions (kg/m<sup>3</sup>) of different mortar mixes.

Type	Sand	Water	Cement	Fly Ash	NS	NT	NF
Control	1250.6	303.4	437.6	187.7	0.0	0.0	0.0
NS1	1250.1	303.2	433.0	187.6	4.4	0.0	0.0
NS3	1249.1	303.0	423.9	187.5	13.1	0.0	0.0
NS5	1248.0	302.7	414.9	187.3	21.8	0.0	0.0
NT1	1251.0	303.5	433.3	187.8	0.0	4.4	0.0
NT3	1251.7	303.6	424.8	187.9	0.0	13.1	0.0
NT5	1252.4	303.8	416.3	188.0	0.0	21.9	0.0
NF1	1251.3	303.5	433.5	187.8	0.0	0.0	4.4
NF3	1252.8	303.9	425.2	188.0	0.0	0.0	13.1
NF5	1254.2	304.3	416.9	188.2	0.0	0.0	21.9

### 2.3. Cement paste

Cement paste specimens with different amounts of nanoparticles were also prepared in order to perform additional experiments. The mixing procedure was the same as mortar mixes except for any aggregates. Seven cement paste specimens were made: reference, specimens with 2%, 4%, and 6% of NS and NT nanoparticles, and specimens with 1%, 3%, 5% of NF nanoparticles. The range of nanoparticles addition in cement pastes is similar to the concentration ranges studied in the mortar.

### 2.4. Testing

#### 2.4.1. Tests performed on mortars

For the fresh properties, workability of the mortars was determined using the standard test method for the flow of hydraulic cement mortar according to [28]. The mechanical properties of the hardened mortar were obtained by performing compressive strength tests in accordance with ASTM C109M-16a [29] and flexural strength test conforming to ASTM C293-02 [30]. Cubic specimens of 50 × 50 × 50 mm for compressive strength and prism specimens of 40 × 40 × 160 mm for flexural strength were used. The microstructure of mortars has been examined using scanning electron microscopy (SEM). Small size samples (max 10 mm length) from mortar specimens were collected from the cube samples. The samples were first coated with a layer of platinum by applying sputter current of 30 mA and sputter time of 40 s using Quorum Q150R S machine. Field-emission scanning electron microscope (FE-SEM, Hitachi SU8010) was used to perform the analyses. Elemental composition in the specimens was measured using EDX (X-max Horiba). Using backscattered electron mode, an accelerating voltage of 15 kV with a magnification of 20,000 was set for all samples.

#### 2.4.2. Tests performed on cement pastes

Mechanical properties of cementitious materials depend, in general, on two things: (micro) mechanical properties of the matrix material (hydration phases including calcium-silicate-hydrate (C-S-H), CH, unhydrated clinker, as well as their proportions) [31] and the porosity/pore size distribution [32]. Therefore, cement pastes with different amounts of nano-particles were tested to quantify their influence on the micro-mechanical properties and the porosity.

To estimate the porosity of cement pastes, porosity accessible to water (sometimes called open porosity) has been measured [33]. Samples were tested at an age greater than 90 days in order to avoid the possible influence of significantly different hydration degrees on the measurement results. Specimens of around 1 cm<sup>3</sup> were cut out from larger specimens to be tested. Per mixture, two specimens were tested and their average is reported. A pre-conditioning procedure has been performed prior to testing. First, the specimens were dried at 105 °C until a constant mass was attained. Then their dry weight ( $m_d$ ) was measured. After drying, the specimens were vacuum saturated with water for 24 h to attain complete saturation. Their saturated-surface-dry (SSD) weight has been measured both in air ( $m_s$ ) and hydrostatically ( $m_h$ ). The apparent porosity ( $\phi$ ) of cement pastes was calculated as [34]:

$$\phi = \frac{m_s - m_d}{m_s - m_h} \quad (1)$$

Micromechanical properties of cement pastes with different amounts of nanoparticles were measured using nanoindentation. Nanoindentation is an advanced characterization technique commonly used to determine local mechanical properties of small volumes from the indentation load/displacement curve [35]. Although originally developed for testing of (relatively) homogeneous materials such as steels and thin films, the technique has gained acceptance in the field of cementitious materials in the past 15 years [36–38]. While the technique can, in principle, be used to determine the micromechanical properties of individual hydration phases in cement paste, using e.g. statistical nanoindentation techniques [39] or in combination with other techniques such as SEM or EDX [40], it is also commonly used to indicate general trends in terms of micromechanical properties of cementitious materials [41,42]. While the latter approach provides less quantitative information, it has the advantage of being simpler (i.e. no additional post-processing of nanoindentation data or testing using other equipment is needed) and more representative of the general microstructure, since larger volumes can be probed.

Hydrated cement pastes with different amounts of nano-additions were used for the testing. Small discs were cut from specimens older than 90 days. The hydration of specimens was stopped using solvent exchange with isopropanol prior to nanoindentation testing [43]. Specimens were submerged five times and taken out for a period of one minute in order to enable a fast exchange of water and the solvent. Afterwards, the specimens were kept in isopropanol until testing. Then, specimens were

ground using sandpaper, using ethanol as a cooling agent to prevent further hydration. Afterwards, the specimens have been polished with 6 μm (5 min), 3 μm (5 min), 1 μm (10 min), and 0.25 μm (30 min) diamond paste on a lapping table. Each polishing step was followed by soaking the specimens in an ultrasonic bath to remove any residue. In general, specimen preparation was performed just prior to nanoindentation testing to avoid possible carbonation of the tested surface.

A KLA-Tencor G200 (KLA, Milpitas, CA, USA) equipped with a Berkovich diamond tip was used for nanoindentation testing. A quartz standard was indented for calibration prior to nanoindentation testing. In each specimen, a series of 20x20 indents were performed on a grid with a spacing of 20 μm between indents. The indentation depth was set to 700 nm. The Continuous Stiffness Method (CSM) developed by Oliver and Pharr [35], which provides a continuous measurement of elastic modulus as a function of indentation depth, was used. The average elastic modulus was determined in the loading range between 500 and 650 nm. Poisson's ratio of the indented material was taken as 0.18 for the calculation.

### 3. Results and discussion

#### 3.1. Mortar

##### 3.1.1. Fresh properties

The fresh properties of the mortar can be affected by the particle size distribution of its constituent materials. Thus, nanoparticles can cause significant alteration to the fresh properties of the mortar due to their extremely small size. The hydraulic flow of mortar is an assessment of the workability of the mortar. Based on Fig. 1, it can be observed that the workability of the mortars does not change dramatically for most tested mixtures compared to the reference. However, the mixture with 5% of NS shows a significant reduction in workability (42.6%) compared to the control mortar mix. At the same dosage, the mixture with NT showed about 10.9% reduction. When the level of nanoparticle dosages exceeded the optimum dosage of 3 wt% of cement, NT showed a gradual decrease in the workability of the fresh mortar whereas NS specimens showed a steep reduction in the workability of the fresh mortar. This may be caused by a much larger specific surface area of NS particles (approximately 6.5 times larger than NT and NF, see Table 1). Mortar with 5% dosages of NF, however, showed improved workability and an increase of about 11% in the slump flow compared to the control mix. This might be due to the higher surface energy of NF compared to NS and NT which could lead to their agglomeration. Nanoparticles have a tendency to

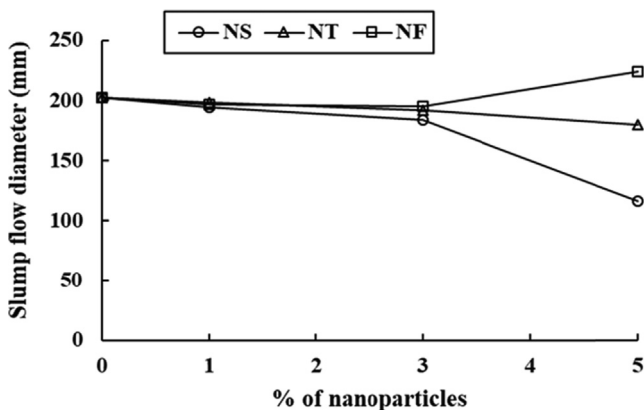


Fig. 1. Effect of the nanoparticles on the slump flow of the mortars.

agglomerate [44], in which case they would have a less pronounced effect on the fresh properties depending on the size and shape of the agglomerates.

##### 3.1.2. Compressive and flexural strengths

The compressive and flexural strengths of the mortars with different percentages of NS, NT, and NF are shown in Fig. 2 and Fig. 3, respectively. It can be observed that both the compressive and the flexural strength increase with a higher dosage of nanoparticles in the mortar. As expected, the strength increases with age as well. In terms of mechanical strength, it seems that the optimum dosage of nanoparticles, at which maximum strength is achieved, is around

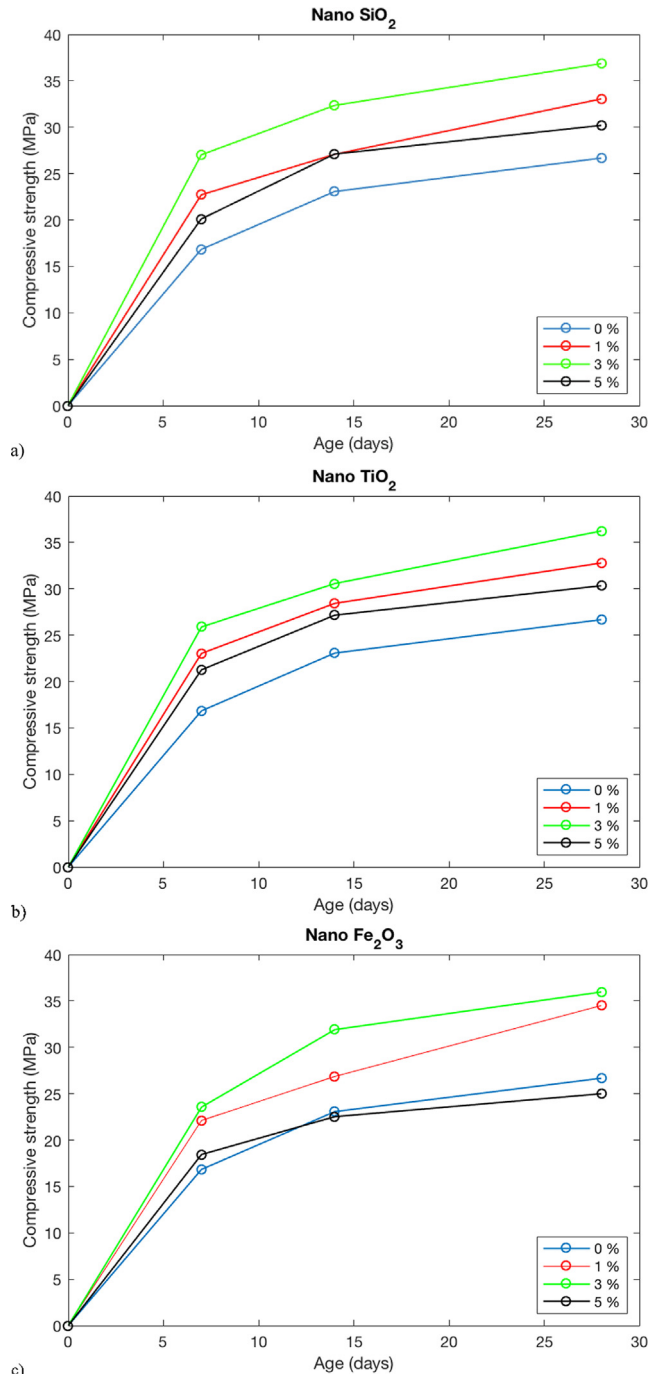
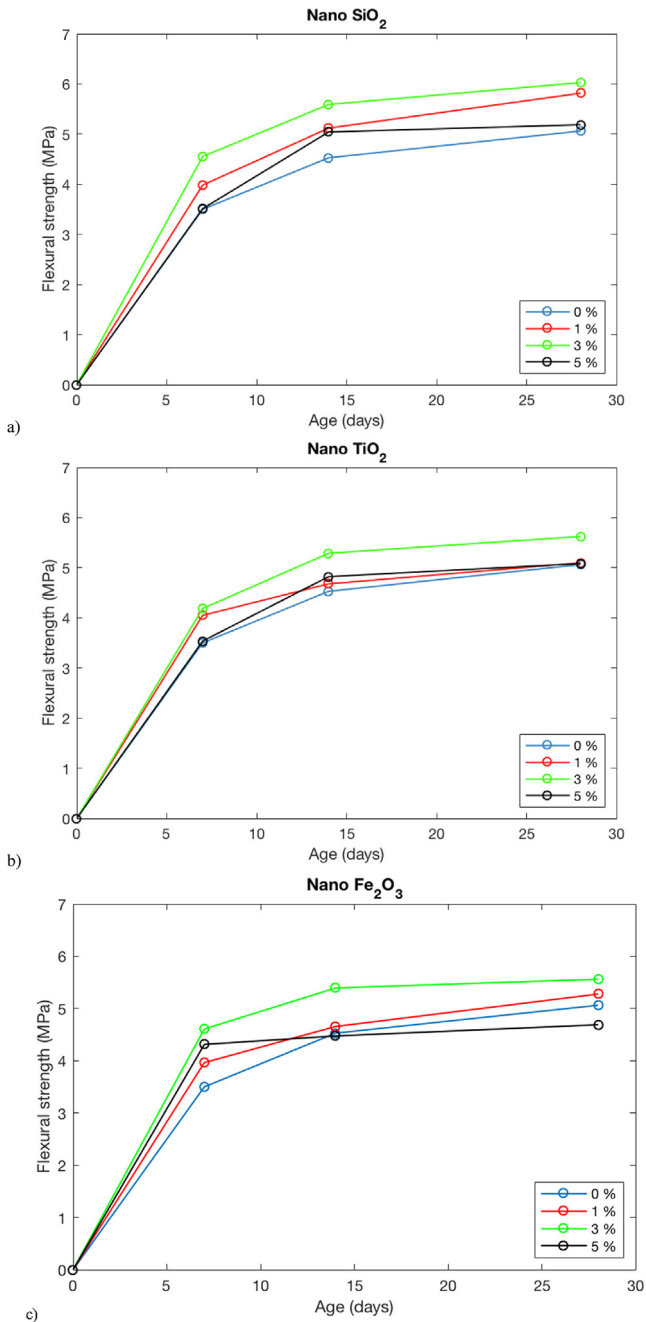


Fig. 2. Effect of various nano-addition percentages on the compressive strength development of mortar: (a) NS, (b) NT, and (c) NF.



**Fig. 3.** Effect of different nano-addition percentages on the flexural strength development of mortar: (a) NS, (b) NT, and (c) NF.

3%. With the 3% dosage of nanoparticles, the 28-day compressive strength is 38%, 36%, and 35% higher in the NS, NT, and NF specimens, respectively, compared to the control specimen. The optimum dosage of NS is also reported to be 3% in a blended cementitious composite [45]. In the case of flexural strength, the increase is 19%, 11%, and 10% in the NS, NT, and NF specimens, respectively, compared to the control specimen. Therefore, the addition of (the right amount of) nanoparticles in cement mortar system shows great potential by significantly improving the mechanical strength properties of the composite.

The addition of nanoparticles in mortars has physicochemical effects. The nanoparticles can increase the rate of hydration of both cement and fly ash due to their small size; they provide additional nucleation sites for the precipitation and development of C-S-H

[17]. High surface activity of nanoparticles as nuclei in mortars can enhance the hydration reaction rate leading to the rapid accumulation of hydration products in the microstructure. As a result, a more uniform distribution of the hydration products can be achieved. In addition, nanoparticles will reduce the amount of free water, and will, therefore, cause denser packing of the particles, thereby reducing the porosity of mortar [46].

Additionally, nanoparticles can work as nanofillers, occupying the pores between cement and fly ash particles, leading to a further reduction in the pore volume of mortars [20]. Nanoparticles can also fill up the pores in the C-S-H gel structure, resulting in a more closely packed structure of hydration products with higher stiffness [47]. Furthermore, the addition of nanoparticles can also reduce the porosity of the ITZ [48], which is known to be the governing parameter (i.e. the “weakest link”) for the mechanical performance of (normal strength) mortar [49,50].

The chemical effect of nanoparticle addition is reflected in its ability to promote an early pozzolanic reaction to occur on their surfaces leading to the formation of C-S-H. This C-S-H typically grows on the surface of the nanoparticles and then serves as the nucleation seeds for the production of C-S-H gel (autocatalysis) [51]. The chemical reaction involved in the growth of these C-S-H particles can be explained by the early pozzolanic reaction of nanoparticles with calcium ions released by the dissolving cement whereby nanoparticles elevate the concentration of the ions which then solvated into the C-S-H gel through the exchange reactions between the dissociated ions from the nanoparticles and the C-S-H gel. Therefore, early strength development of the mortar can further be accelerated [52]. Some researchers have also reported that nanoparticles can reduce the energy threshold required for the nucleation compared to tricalcium silicate (C<sub>3</sub>S) and provide an environment with higher pH value which is suitable for the hydration reactions [53].

Moreover, nanoparticles are able to control the crystallization process of hydration product at an appropriate level. This is due to their ability to reduce the quantity and grain size of the calcium hydroxide (Ca(OH)<sub>2</sub>), and associated reaction that forms C-S-H gel [54]. This enhances the crystal orientation of Ca(OH)<sub>2</sub> between the hardened cement-fly ash paste and the aggregate [55]. Furthermore, Ca(OH)<sub>2</sub> has the highest solubility among the hydration products, thus, it can reduce the durability of the mortars when exposed to water as it may dissolve and increase the porosity of the mortars [51]. Therefore, it is probable that the durability of the mortars is enhanced with the incorporation of nanoparticles.

The increase in strength development can be also caused by the properties of fly ash. In general, the addition of fly ash results in slow strength development at early ages due to its retarded pozzolanic reaction which is much slower than hydration of cement [6]. Reactive silica or alumina from fly ash will react with Ca(OH)<sub>2</sub> generated by the hydration of cement particles to form C-S-H gel in the presence of water [56]. Hence, it is expected that the pozzolanic reaction of fly ash can be escalated with the promotion of the hydration process of cement by incorporation of nanoparticles.

NS has shown the highest improvement of the strength of the mortar followed by NT and NF. This can be explained by the nucleation free energy theory where the number of nucleating points may increase when the size of the particles decreases and the specific surface area increase. For each nucleating point, less energy is required for nucleation. Hence, the nucleation effect is greater for smaller particles and the improvement in the strength is greater [57].

However, the strengths decreased when the incorporation of nanoparticles exceeded 3%. With 5% nanoparticle dosages, the compressive strength at 28 days decreased by 18%, 16%, and 31% for NS, NT and NF specimens, respectively, compared with the

specimens made with 3% dosages. This can be attributed to the fact that nanoparticles contain high surface energy which can lead to agglomeration and uneven dispersion of the nanoparticles in the matrix, thus, leading to the formation of weak zones in the mortars [44]. Moreover, air may infiltrate via vapour-gas nuclei trapped in crevices and produce pores in the matrix [58].

Theoretically, each particle in the mortar possess a cubic pattern and the distance between the particles can be maintained at a suitable length. This is when the nanoparticles are distributed in a uniform manner. The hydrated products are dispersed after the initiation of the cement hydration process and will encircle the nanoparticles as the nucleus instead. It has been shown that when the incorporation of nanoparticles exceeded the threshold quantity, the distance between the particles is reduced. Due to this short distance, the development of  $\text{Ca}(\text{OH})_2$  crystals impede, hence, resulting in insufficient development and the decrease in the quantity of the crystals [23].  $\text{Ca}(\text{OH})_2$  crystals can limit the shrinkage level by acting as a restraint when C-S-H gel collapses after water is eliminated from the pores [51]. Hence, the effect of the agglomeration and non-favourable effect of the nanoparticles on the entire microstructure of the mortar expand the drying shrinkage distortions of mortar which may cause micro cracks to be formed at interfacial transition zone (ITZ). These cracks within the ITZ can cause of lower strengths of the mortar, which has a more pronounced effect on the flexural strength [20]. This is in accordance with the experimental results of the current study: flexural strengths show a higher reduction compared to the compressive strength for specimens with a high amount of nanoparticles (i.e. 5%), especially the NF5 specimens. The decrease in strength of mortar with NS and NF added is comparatively higher than NT. This may due to the fact that NS has a much larger specific surface area than the other nanoparticles. Therefore, more water is bonded by the excess nanoparticles and the availability of water reduces

accordingly, resulting in an incomplete hydration process. At 5% of NS, there is difficulty in compacting the mortar matrix and visible voids were observed in the hardened mortar as the mixture was very dry. This is in accordance with the measurements of workability. It should be noted that no superplasticizer was used in the preparation of mortar mixes in this study. Also, the quantity of NS has exceeded the amount which needed to react with the free lime during the hydration process and may cause the excess nanoparticles to leach out and lead to a reduction in strength [18]. Since better workability was obtained for 5% of NF, the high reduction in strengths might be due to its more intense agglomeration effect compared to NS and NT. Excess nanoparticles may also lead to greater absorption of water and greater agglomeration effect, which results in the formation of undisrupted pores within the paste matrix and higher porosity in the mortars [52].

### 3.1.3. The microstructure of the hardened mortars

The typical SEM images of the reference and NS mortars are discussed here. A reference mortar and specimens with 3% and 5% of NS after 28 days of curing are imaged and shown in Fig. 4. Nanoparticles can enhance the microstructure of the hardened mortar as they can promote the generation of C-S-H gel via accelerated hydration process [52,59,60]. From Fig. 4(a), needle-like ettringite and hexagonal flake of large  $\text{Ca}(\text{OH})_2$  crystals, as well as micropores, can be seen throughout the composite. The microstructure of the reference mortar appeared to be loose and non-homogenous. The morphology of the C-S-H gel which appeared in colloidal form and consists of 4–5 nm elementary spheres seemed to be fibrous and less dense as well.

Fig. 4(b and c) illustrates the specimens with the optimum dosage (3%) of NS incorporated. The microstructure of the specimen appears to be much denser than the reference. Less micropores can be seen between the particles as built-in directional Ca

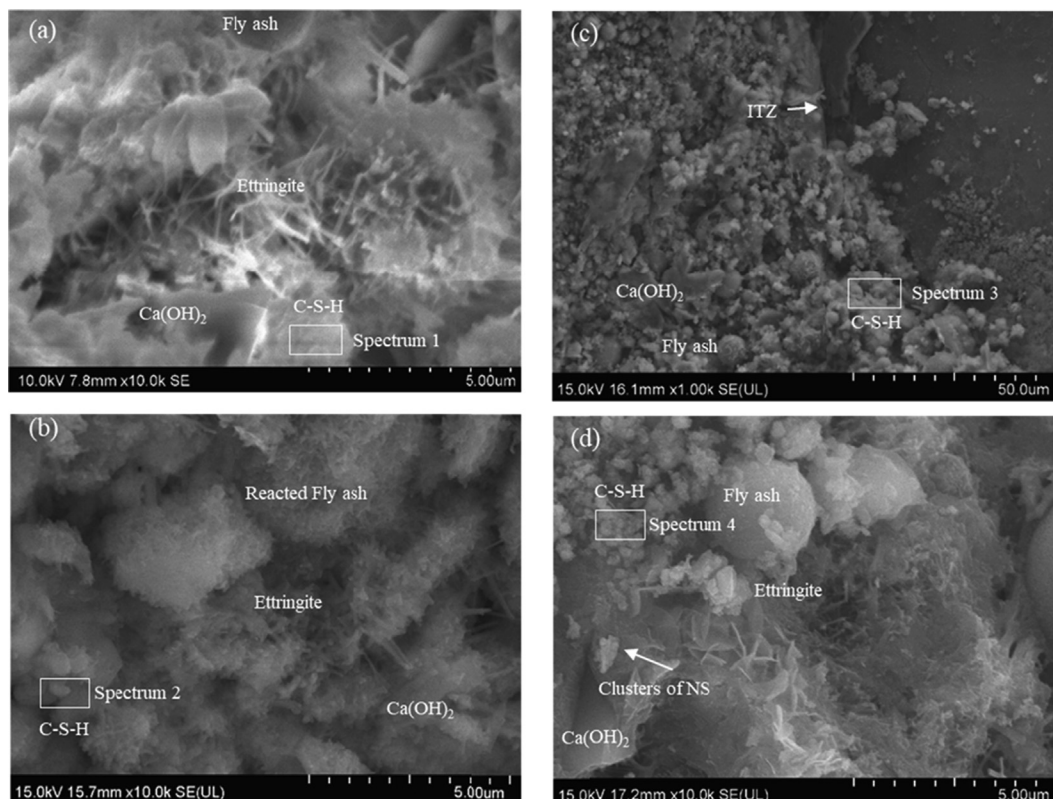
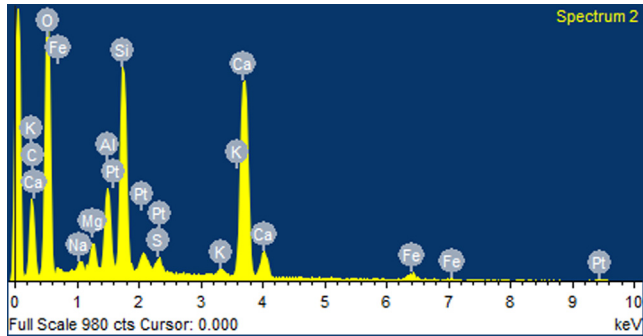


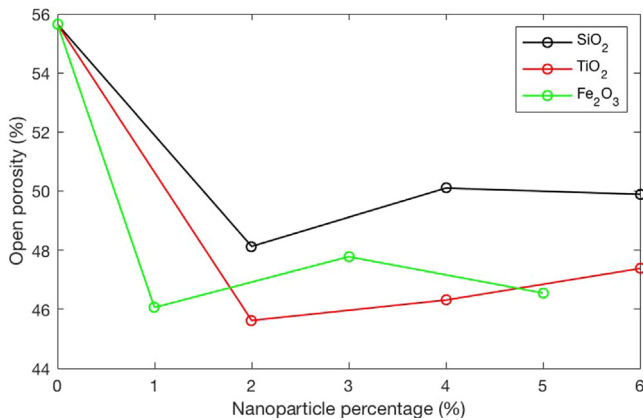
Fig. 4. SEM images of mortar with (a) 0%, (b) 3%, (c) 3% (with ITZ) and (d) 5% of NS.

**Table 3**  
Chemical element compositions of the specimens examined by EDX.

Spectrum	Atomic %				
	C	O	Ca	Si	Ca/Si
1	26.84	57.62	3.81	6.05	0.63
2	39.51	44.82	3.50	5.78	0.61
3	28.17	54.11	5.26	7.71	0.68
4	18.01	63.34	6.29	9.53	0.66

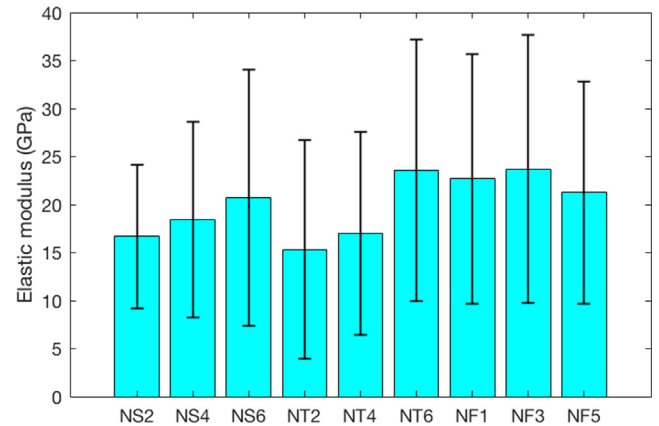


**Fig. 5.** Chemical element compositions of the specimens examined by EDX for spectrum 2.



**Fig. 6.** Porosity accessible to water as a function of nanoparticle percentage in the cement paste. Note that the vertical axis does not start from 0, for easier comparison.

(OH)<sub>2</sub> crystals have been embedded in the pores. A major alteration in the morphology may occur whereby thick ettringite crystals, which mainly form in the pores, may crisscross and interweave with each other to make a complex network which can further reduce the porosity. The porosity tends to decrease with the increase in the percentage of nanoparticles added up to the optimum dosage [20]. Also, the hydration products appear more compact with denser and more structured of C-S-H gel encompassed most of the barite ettringite crystals and hexagonal flake of Ca(OH)<sub>2</sub>. The quantity of large Ca(OH)<sub>2</sub> crystals has reduced tremendously compared to the control specimen. This can be explained by the controlled crystallisation process by nanoparticles. The development of the Ca(OH)<sub>2</sub> crystals may be prevented by the nanoparticles at the appropriate level when the optimum dosage of nanoparticles was added [61]. In addition, nanoparticles can densify the binding paste matrix and enhance the ITZ which is the region between the binding paste and aggregates as shown in Fig. 4(c). ITZ is known to be the weakest link in cement composites [49]. The reaction between the nanoparticles



**Fig. 7.** Average indentation modulus for all analysed paste samples (error bars indicate the standard deviation).

and Ca(OH)<sub>2</sub> crystals may produce more C-S-H gel and fill up the pores and enhance the ITZ [45]. About 1.5 wt% of NS is also reported to condense the ITZ between the matrix and reinforcing substances [62] and significantly improve the fracture properties and mechanical strength.

However, the SEM images for 5% NS in Fig. 4(d) show that more micropores are present and the microstructure of the mortar appears to be less compact compared to the specimen with 3% of NS. There is a noticeable reduction in the interconnections of the hydration products. This is because an excessive amount of nanoparticles can cause them to agglomerate and lead to poor distribution of nanoparticles throughout the matrix, producing weak zones in the mortar [62]. The agglomeration effect can also prevent the nanoparticles from exerting its capability of promoting the hydration reactions. Also, the ITZ has the tendency to increase in size around larger aggregate particles [51]. Thus, the microstructure of the mortar will be negatively affected depending on the level of agglomeration. Yet, the microstructure of specimen with 5% of NS still appeared to be more compact and denser than the control specimens. The microstructures of the samples conform to the strengths obtained for the specimen and nanoindentation results, as shown later.

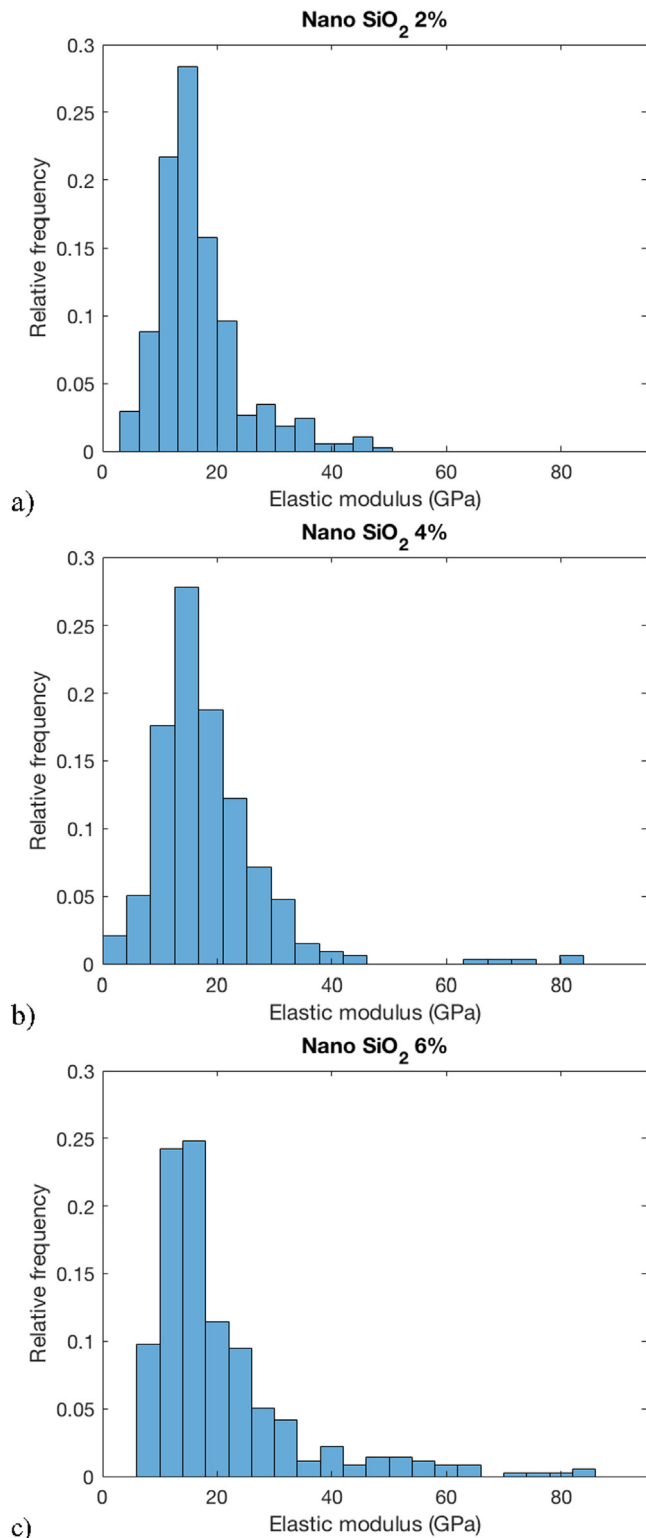
The chemical/elemental compositions of hydration products obtained from the EDX are given in Table 3 and a typical EDX elemental spectrum is presented in Fig. 5. C-S-H gel is the main hydration product that connects all particles together and considered as the main source of mortar strength. The Ca/Si ratio can be varied but the ratio is approximately 0.6 for mortar with fly ash and nanoparticles [20,63].

### 3.2. Cement paste

#### 3.2.1. Open porosity

The influence of nanoparticle addition on the porosity of cement paste (open porosity) is shown in Fig. 6. First, it can be seen that, for all nanoparticles and all concentrations considered, the total open porosity is reduced compared to the porosity of the reference cement paste (with 0% addition of nanoparticles). However, different trends are observed for different nanoparticles. An optimum value is clearly identified in terms of porosity reduction in mortars with all the three nanoparticles. For the NS and the NT particles, clearly, the 2% addition results in the lowest porosity. The porosity increases with the increasing dosages of NS and NT over this 2% optimum dosage, although it remains lower than the porosity of the reference sample. This is in accordance with the strength results measured on mortars, where a similar optimum value (3%)

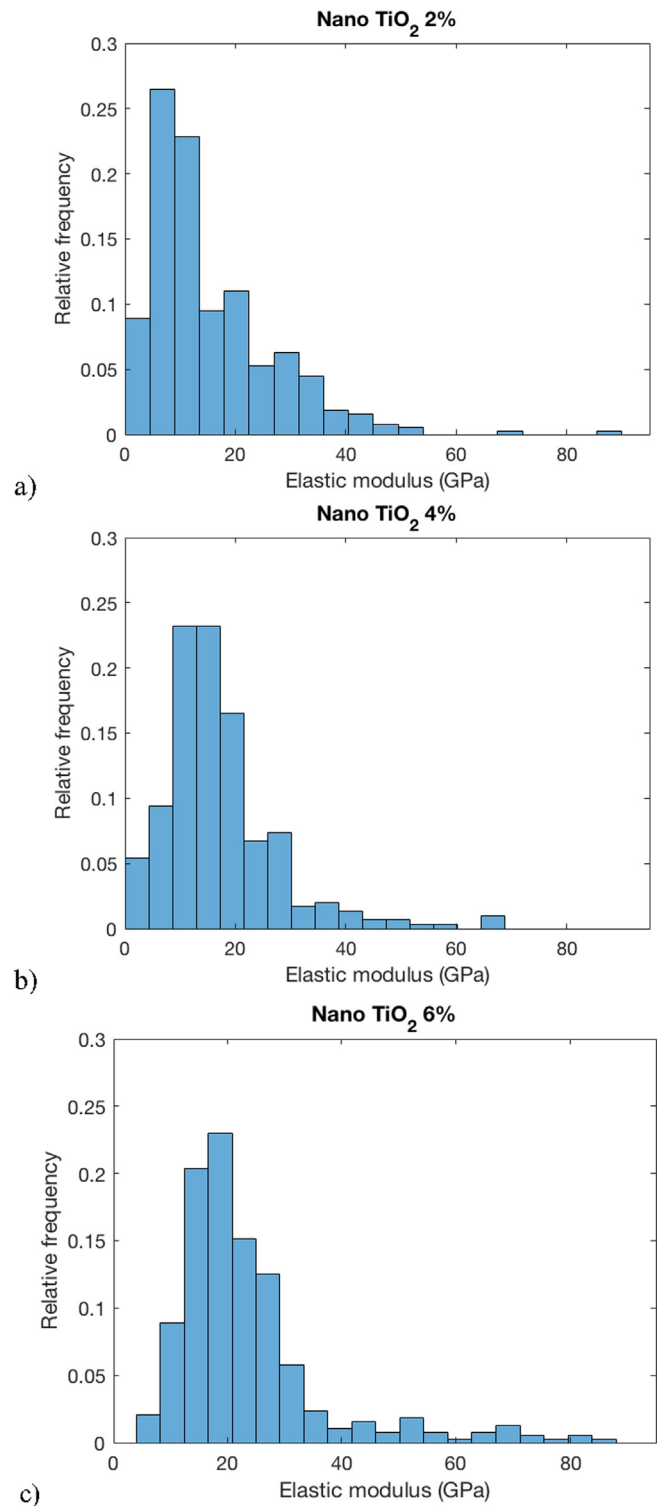




**Fig. 8.** Histograms of indentation moduli for cement pastes with nano-SiO<sub>2</sub>: (a) 2%; (b) 4%; (c) 6%.

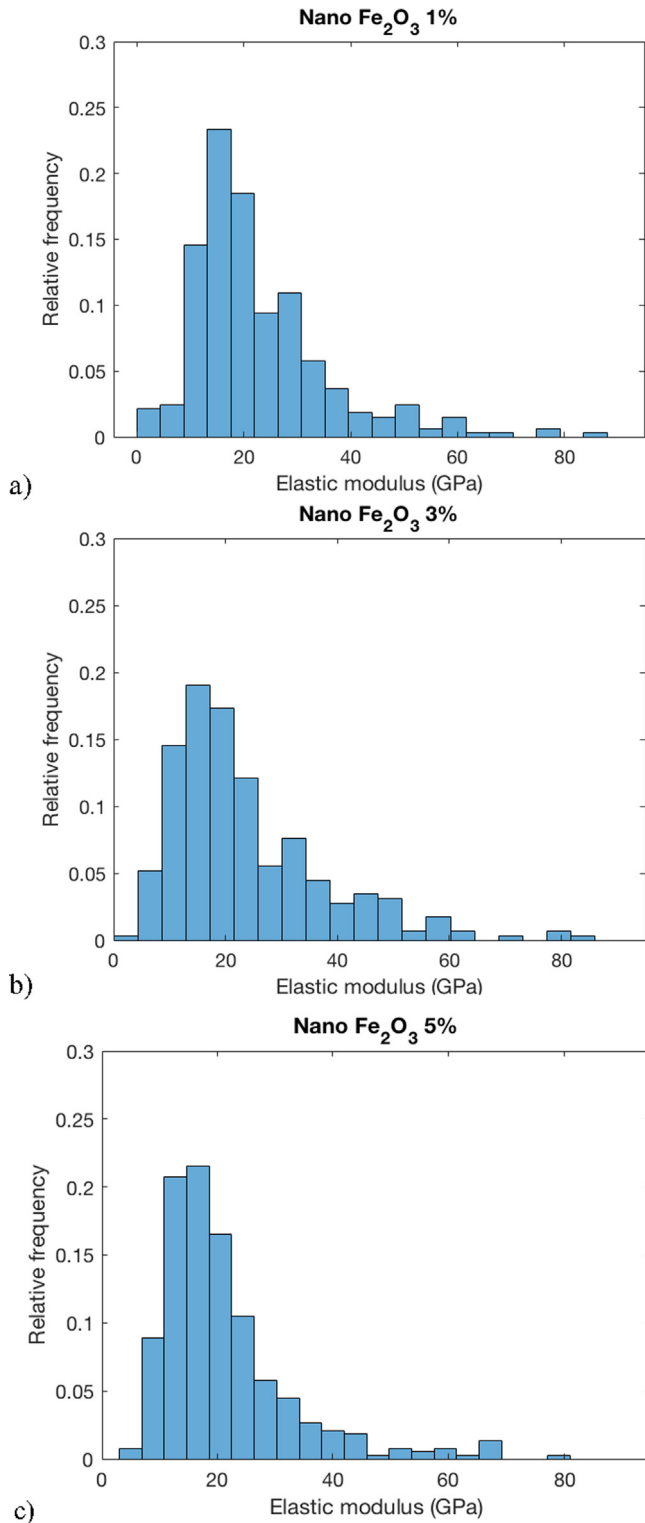
was observed. On the other hand, the lowest porosity is measured for 1% of NF nanoparticle addition in the mortar mix. Since no measurements were performed for the 2% NT addition, it is possible that the optimum is somewhat higher. But, in any case, the porosity at 3% of nanoparticles is higher than the optimum.

There is one difference in terms of the porosity trends at higher dosages of nanoparticles: porosity increases monotonically for the



**Fig. 9.** Histograms of indentation moduli for cement pastes with nano-TiO<sub>2</sub>: (a) 2%; (b) 4%; (c) 6%.

NT specimens with increasing dosages, the porosity in the NS and the NF series at the highest dosage (6% and 5%, respectively) is slightly lower compared to the porosity at intermediate dosages (4% and 3%, respectively). No explanation could be found for this behaviour. It is possible that this is caused in some way by the different particle sizes of nano additions and their dispersion in the cement paste, which is different for different particles. Possible agglomerations could influence the hydration and precipitation



**Fig. 10.** Histograms of indentation moduli for cement pastes with nano-Fe<sub>2</sub>O<sub>3</sub>: (a) 1%; (b) 3%; (c) 5%.

of hydration products at higher dosages, although this has not been studied herein.

### 3.2.2. Nanoindentation results

The average values of indentation modulus are compared and shown for all paste specimens in Fig. 7. Unfortunately, no results are available for the reference specimen (i.e. 0% nanoparticles)

due to experimental malfunction. However, it can be seen that, for the NS and the NT series, the average value of the elastic modulus increases with the increased percentage of nanoparticles in the matrix. The trend is somewhat different for the NF specimen, in which the specimen with the intermediate percentage of nano-additions has the highest average elastic modulus. The average elastic modulus is lower at the maximum concentration (5%) in NF specimen. Nevertheless, the standard deviation is significant and more detail can be seen from individual histograms.

Note that the indentation depth is relatively large (700 nm), so micromechanical properties of individual hydration phases cannot be obtained. Instead, each indent probes a mix of hydration products, unhydrated particles, and/or porosity. While this increases the representativeness of the obtained results, no quantitative comparison with micromechanical properties of individual phases reported in the literature can be made.

Fig. 8, Fig. 9 and Fig. 10 show histograms of measured elastic moduli for the hardened cement paste with various percentages of nanoparticles i.e., NS, NT, and NF series, respectively. For the NS series the left part, represents the hydration products, shifts somewhat to the right with the higher nanoparticle addition. This is probably related to enhanced hydration effect caused by the nanoparticle addition and a possible formation of stiffer hydration products. On the other hand, the histograms also become wider, with more indents with measured high stiffness (>50GPa). This could be caused by insufficient hydration of the cementitious matrix that results in more stiff clinker particles remaining, which, when indented, result in high measured elastic modulus. A similar trend is observed in the NT case. In the case of NF, the average values are quite similar for all NF specimens (see Fig. 8), the histogram does not change significantly with the nanoparticle addition. This could mean that the NF particles interact with the hydration products in a different way compared to the NS and the NT particles. On the other hand, the NF particles could be better distributed in the microstructure at high percentages compared to NS and NT particles (as hypothesized in the section on fresh properties of mortars), without agglomerates. It must be emphasized, again, that the highest percentage of NF tested was 5%, while for the NS and the NT particles it was 6%.

Results from nanoindentation experiments focus on the matrix material (i.e. cement paste), while macroscopic engineering properties are measured on mortars. However, the same mechanisms that influence the strength also seem to affect the micromechanical properties. Also, here, an optimum value of nanoparticle addition seems to be present above which more unhydrated particles remain in the matrix due to agglomeration effects. Understanding of the microstructural and micromechanical effects of nanoparticle additions could help further tailoring such materials.

The addition of nanoparticles has a positive effect on the properties of the ITZ (i.e. strength, stiffness), and this has not been studied herein. However, in order to connect the cement paste scale and the mortar scale, understanding and knowledge of the ITZ region is crucial. This is the governing region for crack initiation since it is usually the weakest link in a cementitious system. Further studies will be performed in this direction.

## 4. Conclusions

In this research, the effects of different types and dosages (1–6%) of nanoparticles on cement pastes and mortars containing 30 wt% fly ash have been investigated. The nanoparticles that were studied are nano-SiO<sub>2</sub> (NS), nano-TiO<sub>2</sub> (NT), and nano-Fe<sub>2</sub>O<sub>3</sub> (NF). The research was focused onto the fresh properties, mechanical properties, and the microstructure of the mortar mix. Nanoparticles exhibit different properties in terms of the size, specific surface area, and different chemical composition and were the main rea-

son for their diverse impact on the properties of mortars investigated.

Based on the investigation performed, the following conclusions can be drawn:

- The addition of nanoparticles has a negative effect on the workability of the fresh mortar with the exception of NF which displays a positive effect with an increase of 10.9% when the excessive dosage (5%) was added. This may be due to the intense agglomeration effect of NF particles.
- The addition of nanoparticles (depending on the dosage) can improve the compressive and flexural strengths of the mortar. However, the agglomeration of nanoparticles can occur if the optimal concentration is exceeded which results in lower mechanical strength.
- Mortars with nanoparticles have a denser and a more compact microstructure compared to reference mortar without the nanoparticles. For the optimum dosage of nanoparticles incorporated, the microstructure appeared to be the most homogeneous and with the lowest porosity present. However, agglomeration of nanoparticles occurred when the percentage of nanoparticles exceeded the optimum dosage. This can lead to the formation of weak zones in the microstructure of the mortar and increase the porosity of the mortar.
- The addition of nanoparticles to cement pastes resulted in a reduction of the open porosity, irrespective of the dosage. The lowest open porosity was found for pastes with 1–3% of nanoparticles, which is in the range of the optimum observed for the mortars.
- The addition of nanoparticles also alters the micromechanical properties of cement pastes. While the average indentation modulus of the pastes increases with the increase of nanoparticle addition, this seems to be caused by the increased amount of unreacted binder particles at concentrations beyond the optimum.

The present study identifies a range of nanoparticle addition that results in an improvement of mechanical properties of cement-fly ash blends for different types of nanoparticles. While mechanisms of this have been discussed, further research is needed to clarify this. Furthermore, while the current study looked at the cement paste and the mortar, the influence of nanoparticle addition on the ITZ in cement-fly ash blends has not been studied. This also has an important effect on mechanical performance. Finally, it is also possible that, with a better method of dispersion, even higher amounts of nanoparticles than the optimum found here could be used. This is also an area where further research is needed.

#### CRedit authorship contribution statement

**Ding Siang Ng:** Methodology, Investigation, Writing - original draft, Visualization. **Suvash Chandra Paul:** Supervision, Methodology, Conceptualization, Writing - original draft. **Vivi Anggraini:** Supervision, Writing - review & editing. **Sih Ying Kong:** Writing - review & editing. **Tanvir Shams Qureshi:** Writing - review & editing. **Claudia Romero Rodriguez:** Investigation, Writing - review & editing. **Qing-feng Liu:** Writing - review & editing. **Branko Šavija:** Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### References

- [1] C. Li, X.Z. Gong, S.P. Cui, Z.H. Wang, Y. Zheng, B.C. Chi, CO<sub>2</sub> emissions due to cement manufacture. *Materials Science Forum: Trans Tech Publ*; 2011. p. 181–187.
- [2] B. Lothenbach, K. Scrivener, R. Hooton, Supplementary cementitious materials. *Cem. Concr. Res.* 41 (2011) 1244–1256.
- [3] M.C. Juenger, R. Siddique, Recent advances in understanding the role of supplementary cementitious materials in concrete. *Cem. Concr. Res.* 78 (2015) 71–80.
- [4] R. Snellings, G. Mertens, J. Elsen, Supplementary cementitious materials. *Rev. Mineral. Geochem.* 74 (2012) 211–278.
- [5] S. Hanehara, F. Tomosawa, M. Kobayakawa, K. Hwang, Effects of water/powder ratio, mixing ratio of fly ash, and curing temperature on pozzolanic reaction of fly ash in cement paste. *Cem. Concr. Res.* 31 (2001) 31–39.
- [6] J. Feng, J. Sun, P. Yan, The influence of ground fly ash on cement hydration and mechanical property of mortar. *Adv. Civil Eng.* 2018 (2018).
- [7] C. Poon, L. Lam, Y. Wong, A study on high strength concrete prepared with large volumes of low calcium fly ash. *Cem. Concr. Res.* 30 (2000) 447–455.
- [8] G.L. Golewski, An assessment of microcracks in the Interfacial Transition Zone of durable concrete composites with fly ash additives. *Compos. Struct.* 200 (2018) 515–520.
- [9] G.L. Golewski, Evaluation of morphology and size of cracks of the Interfacial Transition Zone (ITZ) in concrete containing fly ash (FA). *J. Hazard. Mater.* 357 (2018) 298–304.
- [10] J. Branch, R. Epps, D. Kosson, The impact of carbonation on bulk and ITZ porosity in microconcrete materials with fly ash replacement. *Cem. Concr. Res.* 103 (2018) 170–178.
- [11] J. Szymanowski, Ł. Sadowski, Functional and adhesive properties of cement-based overlays modified with amorphous silica nanospheres. *J. Adhes.* 96 (2020) 207–228.
- [12] J. Szymanowski, Ł. Sadowski, The influence of the addition of tetragonal crystalline titanium oxide nanoparticles on the adhesive and functional properties of layered cementitious composites. *Compos. Struct.* 233 (2020) 111636.
- [13] M. Wiesner, J.-Y. Bottero, *Environmental Nanotechnology*, McGraw-Hill Professional Publishing, New York, 2007.
- [14] M. Oltulu, R. Şahin, Effect of nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub> and nano-Fe<sub>2</sub>O<sub>3</sub> powders on compressive strengths and capillary water absorption of cement mortar containing fly ash: a comparative study. *Energy Build.* 58 (2013) 292–301.
- [15] S. Kawashima, P. Hou, D.J. Corr, S.P. Shah, Modification of cement-based materials with nanoparticles. *Cem. Concr. Compos.* 36 (2013) 8–15.
- [16] S.P. Shah, P. Hou, M.S. Konsta-Gdoutos, Nano-modification of cementitious material: toward a stronger and durable concrete. *J. Sustainable Cem.-Based Mater.* 5 (2016) 1–22.
- [17] P. Hou, K. Wang, J. Qian, S. Kawashima, D. Kong, S.P. Shah, Effects of colloidal nano-SiO<sub>2</sub> on fly ash hydration. *Cem. Concr. Compos.* 34 (2012) 1095–1103.
- [18] E. Mohseni, B.M. Miyandehi, J. Yang, M.A. Yazdi, Single and combined effects of nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub> and nano-TiO<sub>2</sub> on the mechanical, rheological and durability properties of self-compacting mortar containing fly ash. *Constr. Build. Mater.* 84 (2015) 331–340.
- [19] E. Mohseni, M.M. Ranjbar, M.A. Yazdi, S.S. Hosseiny, E. Roshandel, The effects of silicon dioxide, iron (III) oxide and copper oxide nanomaterials on the properties of self-compacting mortar containing fly ash. *Mag Concr Res.* 67 (2015) 1112–1124.
- [20] L. Wang, D. Zheng, S. Zhang, H. Cui, D. Li, Effect of nano-SiO<sub>2</sub> on the hydration and microstructure of Portland cement. *Nanomaterials.* 6 (2016) 241.
- [21] L. Senff, J.A. Labrincha, V.M. Ferreira, D. Hotza, W.L. Repette, Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. *Constr. Build. Mater.* 23 (2009) 2487–2491.
- [22] S.C. Paul, A.S. van Rooyen, G.P. van Zijl, L.F. Petrik, Properties of cement-based composites using nanoparticles: a comprehensive review. *Constr. Build. Mater.* 189 (2018) 1019–1034.
- [23] N.A. Yazdi, M. Arefi, E. Mollaahmadi, B.A. Nejand, To study the effect of adding Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the morphology properties and microstructure of cement mortar. *Life Sci. J.* 8 (2011) 550–554.
- [24] M. Harilal, V. Rathish, B. Anandkumar, R. George, M.H.S. Mohammed, J. Philip, et al., High performance green concrete (HPGC) with improved strength and chloride ion penetration resistance by synergistic action of fly ash, nanoparticles and corrosion inhibitor. *Constr. Build. Mater.* 198 (2019) 299–312.
- [25] M. Jalal, M. Fathi, M. Farzad, Effects of fly ash and TiO<sub>2</sub> nanoparticles on rheological, mechanical, microstructural and thermal properties of high strength self compacting concrete. *Mech. Mater.* 61 (2013) 11–27.
- [26] F.U. Shaikh, S.W. Supit, Mechanical and durability properties of high volume fly ash (HVFA) concrete containing calcium carbonate (CaCO<sub>3</sub>) nanoparticles. *Constr. Build. Mater.* 70 (2014) 309–321.
- [27] S.W.M. Supit, F.U.A. Shaikh, Durability properties of high volume fly ash concrete containing nano-silica. *Mater. Struct.* 48 (2015) 2431–2445.
- [28] ASTM. C1437-07. Standard Test Method for Flow of Hydraulic Cement Mortar. 2019.
- [29] ASTM. C109/C109M-16a. Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens). 2019.
- [30] ASTM. ASTM C293-02. Standard Test Method for Flexural Strength of Concrete (Using Simple Beam With Center-Point Loading). 2019.

- [31] B. Šavija, H. Zhang, E. Schlangen, Assessing hydrated cement paste properties using experimentally informed discrete models, *J. Mater. Civ. Eng.* 31 (2019) 04019169.
- [32] D. Liu, B. Šavija, G.E. Smith, P.E. Flewitt, T. Lowe, E. Schlangen, Towards understanding the influence of porosity on mechanical and fracture behaviour of quasi-brittle materials: experiments and modelling, *Int. J. Fract.* 205 (2017) 57–72.
- [33] M. Krus, K.K. Hansen, H. Künzel, Porosity and liquid absorption of cement paste, *Mater. Struct.* 30 (1997) 394–398.
- [34] C.R. Rodriguez, França de Mendonça, F. Filho, S. Chaves, Figueiredo, E. Schlangen, B. Šavija, Fundamental investigation on the frost resistance of mortar with microencapsulated phase change materials. *Cement and Concrete Composites*. Submitted for publication.
- [35] W.C. Oliver, G.M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: advances in understanding and refinements to methodology, *J. Mater. Res.* 19 (2004) 3–20.
- [36] G. Constantinides, F.-J. Ulm, K. Van Vliet, On the use of nanoindentation for cementitious materials, *Mater. Struct.* 36 (2003) 191–196.
- [37] M. Luković, B. Šavija, H. Dong, E. Schlangen, G. Ye, Micromechanical study of the interface properties in concrete repair systems, *J. Adv. Concr. Technol.* 12 (2014) 320–339.
- [38] F.-J. Ulm, M. Vandamme, H.M. Jennings, J. Vanzo, M. Bentivegna, K.J. Krakowiak, et al., Does microstructure matter for statistical nanoindentation techniques?, *Cem. Concr. Compos.* 32 (2010) 92–99.
- [39] L. Sorelli, G. Constantinides, F.-J. Ulm, F. Toutlemonde, The nano-mechanical signature of ultra high performance concrete by statistical nanoindentation techniques, *Cem. Concr. Res.* 38 (2008) 1447–1456.
- [40] W. Wilson, L. Sorelli, A. Tagnit-Hamou, Automated coupling of NanoIndentation and Quantitative Energy-Dispersive Spectroscopy (NI-QEDS): a comprehensive method to disclose the micro-chemo-mechanical properties of cement pastes, *Cem. Concr. Res.* 103 (2018) 49–65.
- [41] O. Çopuroğlu, E. Schlangen, Modeling of frost salt scaling, *Cem. Concr. Res.* 38 (2008) 27–39.
- [42] B. Šavija, H. Zhang, E. Schlangen, Influence of microencapsulated phase change material (PCM) addition on (micro) mechanical properties of cement paste, *Materials* 10 (2017) 863.
- [43] J. Zhang, G.W. Scherer, Comparison of methods for arresting hydration of cement, *Cem. Concr. Res.* 41 (2011) 1024–1036.
- [44] D. Kong, X. Du, S. Wei, H. Zhang, Y. Yang, S.P. Shah, Influence of nano-silica agglomeration on microstructure and properties of the hardened cement-based materials, *Constr. Build. Mater.* 37 (2012) 707–715.
- [45] K. Snehal, B. Das, M. Akanksha, Early age, hydration, mechanical and microstructure properties of nano-silica blended cementitious composites, *Constr. Build. Mater.* 233 (2020) 117212.
- [46] M. Ltifi, A. Guefreh, P. Mounanga, A. Khelidj, Experimental study of the effect of addition of nano-silica on the behaviour of cement mortars, *Procedia Eng.* 10 (2011) 900–905.
- [47] P. Mondal, S.P. Shah, L.D. Marks, J.J. Gaitero, Comparative study of the effects of microsilica and nanosilica in concrete, *Transp. Res. Rec.* 2141 (2010) 6–9.
- [48] A. Nazari, S. Riahi, The effect of TiO<sub>2</sub> nanoparticles on water permeability and thermal and mechanical properties of high strength self-compacting concrete, *Mater. Sci. Eng., A* 528 (2010) 756–763.
- [49] J.G. Van Mier, *Fracture Processes of Concrete*, CRC Press, 2017.
- [50] H. Zhang, Y. Gan, Y. Xu, S. Zhang, E. Schlangen, B. Šavija, Experimentally informed fracture modelling of interfacial transition zone at micro-scale, *Cem. Concr. Compos.* 104 (2019) 103383.
- [51] J.J. Thomas, H.M. Jennings, J.J. Chen, Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, *J. Phys. Chem. C* 113 (2009) 4327–4334.
- [52] J. Chen, S.-c. Kou, C.-s. Poon, Hydration and properties of nano-TiO<sub>2</sub> blended cement composites, *Cem. Concr. Compos.* 34 (2012) 642–649.
- [53] T. Oey, A. Kumar, J.W. Bullard, N. Neithalath, G. Sant, The filler effect: the influence of filler content and surface area on cementitious reaction rates, *J. Am. Ceram. Soc.* 96 (2013) 1978–1990.
- [54] L. Singh, S. Karade, S. Bhattacharyya, M. Yousuf, S. Ahalawat, Beneficial role of nanosilica in cement based materials—a review, *Constr. Build. Mater.* 47 (2013) 1069–1077.
- [55] T. Ji, Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO<sub>2</sub>, *Cem. Concr. Res.* 35 (2005) 1943–1947.
- [56] W. Ma, P.W. Brown, Hydrothermal reactions of fly ash with Ca(OH)<sub>2</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O, *Cem. Concr. Res.* 27 (1997) 1237–1248.
- [57] Z. Li, J. Wang, Y. Li, X. Yu, B. Han, Investigating size effect of anatase phase nano TiO<sub>2</sub> on the property of cement-based composites, *Mater. Res. Express* 5 (2018) 085034.
- [58] X. Wang, Effects of nanoparticles on the properties of cement-based materials, 2017.
- [59] P. Hosseini, A. Booshehrian, S. Farshchi, Influence of nano-SiO<sub>2</sub> addition on microstructure and mechanical properties of cement mortars for ferrocement, *Transp. Res. Rec.* 2141 (2010) 15–20.
- [60] A.M. Said, M.S. Zeidan, M. Bassuoni, Y. Tian, Properties of concrete incorporating nano-silica, *Constr. Build. Mater.* 36 (2012) 838–844.
- [61] H. Feng, Z. Wang, M.N. Sheikh, X. Zhao, D. Gao, M.N. Hadi, The effect of nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, and nano-Fe<sub>2</sub>O<sub>3</sub> on the compressive strength and workability of magnesium phosphate cement-based mortar, *Adv. Civil Eng. Mater.* 8 (2019) 192–208.
- [62] J. Yu, M. Zhang, G. Li, J. Meng, C.K. Leung, Using nano-silica to improve mechanical and fracture properties of fiber-reinforced high-volume fly ash cement mortar, *Constr. Build. Mater.* 239 (2020) 117853.
- [63] W. Kunther, S. Ferreiro, J. Skibsted, Influence of the Ca/Si ratio on the compressive strength of cementitious calcium-silicate-hydrate binders, *J. Mater. Chem. A* 5 (2017) 17401–17412.