Single and combined impact of silica fumes with Functionalized multi-walled carbon Nanotubes and nano silica on performance of cement mortars composites

Ibrahim M. El-Kattan1*, M H Khedr 2, A A Farghali 2, M Elsaeidy 3 and F N Soliman5, 6

1Environmental Science and Industrial Development Department, Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University, Beni-Suef 62511, Egypt
2Material Sciences and Nano Technology Department, Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University, Beni-Suef 62511, Egypt.
3Wadi El Nile Cement Company, Beni-Suef, Egypt.

*E-mail: ibrahim.elkattan@psas.bsu.edu.eg

Abstract. This present work aims to study the impact of single and combined effects of silica fumes (SF) with nano silica (NS) and functionalized multi walled carbon Nanotubes (MWCNTs) on physicomechanical and dynamic properties of cement mortars (CMs). The Portland cement (PC) was partially substituted with different ratios of SF, MWCNTs and NS which, firstly was individually substituted but Secondly, were added together. PC was individually substituted with 2, 4, 6, 8, 10 wt. % of SF then combined with 0.2, 0.4, 0.6, 0.8 and 1.0 wt. % of MWCNTs and 2, 4, 6, 8, 10 wt. % of NS which mixing together. The physicomechanical and dynamic properties such as compressive strength, bending strength, water consistency; both initial and final setting times were measured. The phases of hydration products of some selected samples were additionally investigated by using XRD analyses, the morphology of hardened samples was studied by SEM techniques and TEM showed the particle size of nanoparticles. The results illustrated that, the compressive strength of cement mortars (CM) which containing SF increasing by 27% at 28days and 11% for bending strength at early ages comparing to control sample. In combination with functionalized MWCNTS, the compressive and bending strengths increased by 36 and 17% in case of CMs that containing 0.4 Wt.,% functionalized MWCNTs and 8 Wt.,% SF. Additionally, the combination of SF with NS showed increment in compressive strength by 28% at 8 Wt.,% SF and 8 Wt.,% NS, respectively. SEM-photos showed that CMs containing 0.4 Wt., % functionalized MWCNTs and 8 Wt., % SF had more compacting microstructure than control sample due to bridging effect of MWCNTs and pozzolanic effect of SF.

1. Introduction
Particles with ranging lengths from 1 to 100 nm are non-materials. Cement is a fine powder acting as a hydraulic binder, i.e. a finely ground clinker and additives which, when mixed with water; forms a cement paste which hardens and sets through hydration reactions and after setting, retains its strength and stability even under water. Recently; the beneficial role of nano-materials in cement field greatly increased [1]. The cement paste matrix is in itself a multi-phase material. Basically, it is a porous...
material composed of calcium hydroxide (portlandite), aluminates and un-hydrated clinker embedded into an amorphous nanostructured hydration product, the so-called C–S–H gel [2]. The major most important constituent of hydrated cement (50–70%, v/v) is calcium silicates which is produced on two stages; a first then a second hydration stages resulting in low then high density hydrated phase, respectively whose mechanical properties and characteristics were reported by nano-indentation experiments [4].

Silica fume (SF), is a by-product of ferrosilicon industry known as pozzolanic material consists of small (≈100 nm) spherical shaped amorphous silica. SF was reported to increases cement strength and improves mechanical properties when mixed with optimum reported replacement of 7.5 to 10 W% to Portland cement [5-7] and predominating was investigated at 10% [8]. Studies about using SF in high strength concrete were reported along 40 years [9] showing higher compressive strengths than 100 MPa. Strengths more than 150 MPa were reported [10–12]. Advantages of SF as a replacement of cement include: Higher compressive strength with the same plant cement mix design parameters; lower cement content for a desired strength; and higher concrete durability [13–17].

Carbon nanotubes (CNTs) show two specific morphologies [18], a graphene sheet rolled singly on a cylinder known as single-walled nanotubes and multi concentric graphene sheets cylinders of nanometer and micron scales of diameters and scale lengths, respectively [19] as presented in figure 1. Those characteristics made them excellent future carbon fibers substitutes [18]; being light, strong, and can withstand bending with no torsions and breaking [20, 21]. Single walled nanotubes have Young’s modulus theoretically calculated TPa range from 1 to 5 [22-24] compared to carbon fibers of 400 GPa meaning that CNTs are with very high tensile strength compared to carbon fibers. Additionally, CNTs are electrically and thermally conductive (1000 times greater conductivity than copper and can withstand up to 2800 °C under vacuum [25], so, they are applicable as conductors and semiconductors [18].

An oxidative treatment is performed for MWNTs synthesized in presence of a catalyst for functionalizing their surface; oxidation is performed using a mixture of concentrated nitric acid and sulfuric acid solution. Modifications of structural integrity may result due to uncontrolled conditions. The optimum surface functionalization conditions minimum nanotubes damage and maximum surface carboxylic groups (~28%) are 18 hr. treatment with 4.0 M HNO₃:10.0 M H₂SO₄ (1:3, v/v) [18], the functionalized MWCNTs were presented in (figure 1).

![Figure 1. Illustration of MWCNTs and activated MWCNTs](image.png)

The dispersion of non-functionalized CNTs in cement paste was reported to be done using ultrasonic mixing in presence of aqueous surfactant at specific time using dispersion energy. Zou et al. stated ultrasonication energy nearly 20 J/mL per unit CNTs to cement for 84% dispersion [26]. Using high force might may dissolve CNTs or destroy CNTs, also incompatibility of surfactants affects on setting time [27]. Chemical activation is a process of creating functional groups on MWCNTs surface to enhance bonding and dispersion with matrix. Chemical activation is reported to be processed by applying ozone gas with high temperature then acid treatment lead to carboxyl groups to improve bonding with cement particles by formation of chemical reactions. Kang et al. stated the same strategy but without using surfactants [28]. Studying the effect of Nano Silica (NS) and CNTs on the properties of cement based materials revealed contradictory results, about the effect of NS on the hydration degree of cement; some papers showed an increase at the first hours [29, 30], while others showed a decrease in setting time.
compared to plain paste [31]. NS effect on the mechanical properties were discrepant; some showed increase [30, 32] and others reported insignificant influence [33] finally a decrease in compressive strength [34, 35] compared to blank cement samples. The latest papers was performed to synthesize the functionalized MWCNTs and studying their effect on Physico-mechanical characteristics of cement mortar [28] by using harmful greenhouse gas (ozone) and higher temperature which is consuming energy [36]. For clarification, the reported results, the surface area and type of the used NS have a different effect on physio-mechanical properties with cement composites [37]. All the up to date reported studies either using NS or MWCNTs did not follow the EN 197-1/2011 standards or any other standards [38]. Recent time, Using of nanoparticles in cement manufacturing and concrete (as substitution) leads to sustainable cement, concrete design and green environment [48].

The main objective of the present work is studying, the single and dual effect of SF with functionalized MWCNTS and NS on dynamic and physico-mechanical properties of cement mortars (CMs). The MWCNTs were functionalized without using of greenhouse gases or energy consuming temperature [36]. The NS was performed by using commercial precipitation method. Different experimental and instrumental techniques were conducted to evaluate the behaviour of CMs. Physico-mechanical and dynamic properties such as compressive strength, bending moment, water consistency, initial setting time and final setting time were conducted to evaluate the performance of CMs. The results of this paper confirmed that, the modification of PC- properties with nanoparticles decreased the global environmentally harmful carbon dioxide emissions combined with cement industry [39].

2. Experimental

2.1. Synthesis, purification, characterization, and functionalization of multi-walled carbon nanotubes (MWCNTs) by thermal chemical vapor deposition (CVD)

Synthesis of MWCNTs in presence of Co-Fe/CaCO3 catalyst, characterized by TEM (figure 2) [40], was performed at 600 °C for 30 minutes using commercial acetylene gas cylinder, a procedure reported to be of a high MWCNTs yield [40]. By energy, acetylene molecules were cracked into reactive atomic carbon which diffused into the substrate, which was then heated and coated with the catalyst. CVD used in the synthesis was presented as diagram in (figure 3). After purification, functionalized using Conc. H2SO4 and HNO3 was performed [40]. The produced MWCNTs were investigated by TEM before (figure 4) and after (figure 5) purification and by XRD (figure 6). TEM for functionalized MWCNT shows the dispersion and the absence of impurities as catalyst particles. The crystal structure and phases of the prepared Functionalized MWCNT were scanned by X-ray diffraction (XRD, PANalytical Empyrean) with scanning range from 5° to 80°, the detector step size was 0.03°, and the step time was 0.3 s, the diffract meter applied is Cu Kα radiation with the wavelength of 1.54060 Å and the Generator Settings operated at 40 KV and 30 mA with scanning type, continuous. XRD for Functionalized MWCNT showed that the crystal size is 7.8 nm which had been calculated automatically by the XRD instrument using Debye sherrer formula.

2.2. Synthesis and characterization of precipitated nanosilica (NS)

Conc. HCl was added drop wisely added to sodium silicate solution with constant stirring to at room temperature (21-24 °C). When it’s 8-9 pH; silica gel are formed which are aged for 24 h. at room temperature, filtered, washed several times with water till absence of chloride tested by silver nitrate, then dried at 90 °C for 18 hrs., finally ground in a ball mill for 2 hrs.. [41] then characterization by TEM (figure 7) shows that NS is amorphous as characterized by XRD (figure 8), the particle size ranged from 41 - 102 nm as characterized in SEM (figure 9). XRF (table. 1) showed that the silica content is nearly 91%. TEM of NS (figure 7) confirmed that a spherical morphology of almost particles with low aggregation. The TEM proved that, NS particles have an average diameter from 41 nm to 102 nm. The TEM photos reported that the crystals are mostly angular with slightly elongated shape. The light pattern showing bright points and rings supported the amorphous structure of NS particles which was previously
confirmed by the XRD pattern for amorphous NS (figure 8) which showed a typical broad peak which was corresponding to the amorphous phase of NS particles. Peak broadness may be due to the small size and incomplete inner structure of the prepared particles. This proved that a high percentage of amorphous particles. SEM micrograph revealed that the average particle size of powdered-NS ranged from 41 nm to 102 nm and the particles are spherical, non-agglomerated and possess a smooth surface morphology (figure 9). XRF (table 1) showed that the silica content is nearly 91%.

![Figure 2. TEM-photos of the catalyst (Co-Fe/CaCO₃) used for MWCNTs preparation.](image)

![Figure 3. Schematic diagram of thermal CVD apparatus.](image)
Figure 4. TEM-photos of the MWCNTs prepared by CVD before purification and functionalization.

Figure 5. TEM-photos of the purified and functionalized MWCNTs.
Figure 6. XRD-pattern of the prepared Functionalized MWCNTs.

Figure 7. TEM-photos and particle light diffraction for the precipitated amorphous nano silica (NS).

Figure 8. XRD pattern for the precipitated amorphous Nano Silica (NS).
2.3. Characterization of SF

The purchased SF from Sika Egypt for Construction Chemicals Co., was characterized by XRF showed in table 2 with SiO$_2$% content 88.48%. XRD showed amorphous SF (figure 10) TEM as shown in figure 11, shows particles diameter ranges from 50 to 150 nm.

2.4. Samples preparation

Portland Cement (PC) CEM I (42.5 N) used as a blank cement type in the suggested study is complying with BS EN 197-1/2011 [38] produced by Wadi El Nile Cement Company, Egypt, the physical and chemical analysis of the used plain CEM I (42.5 N) was represented in table 2 and XRD characterization was shown in figure 12. Cement was mixed in different ratios with, SF at first, and then both SF and functionalized MWCNTs, and finally both SF with NS for preparing samples to be tested, the summarized nominations and mix design of prepared samples were represented in table 3.

Table 2. XRF analysis of the silica fumes (SF).

| SiO$_2$% | Al$_2$O$_3$% | Fe$_2$O$_3$% | CaO% | MgO% | SO$_3$% | K$_2$O% | Na$_2$O% | Chloride % |
|---------|-------------|-------------|------|------|---------|--------|---------|-----------|
| 88.48   | 1.44        | 1.68        | 0.07 | 0.38 | 0.10    | 0.47   | 0.54    | 0.003     |

Figure 10. XRD-pattern for the used silica fumes (SF).
Figure 11. TEM-photos for Silica Fumes (SF).

Figure 12. XRD-pattern of the used plain CEM I (42.5 N).

Table 3. Chemical and physical analysis of CEM I (42.5 N) according to European Standard: Cement Composition 2011.

| Component       | Value       | Component       | Value       | Component       | Value       |
|-----------------|-------------|-----------------|-------------|-----------------|-------------|
| SiO₂%           | 19.67       | Na equivalent   | 0.77        | Wet Chloride (%)| 0.05        |
| Al₂O₃%          | 4.96        | LSF             | 99.33       | Wet Free CaO (%)| 1.46        |
| Fe₂O₃%          | 3.64        | SIM             | 2.29        | Insoluble Residue| 0.60        |
| CaO%            | 62.85       | ALM             | 1.36        | 45µ (%)         | 18.70       |
| MgO%            | 1.16        | C3S %           | 52.44       | 90µ(%)          | 1.80        |
| SO₃%            | 2.82        | C2S %           | 16.84       | Blaine (cm²/m)  | 3018        |
| K₂O%            | 0.288       | C3A %           | 7.36        | Soundness (mm)  | 0.00        |
| Na₂O%           | 0.58        | C4AF %          | 11.06       | Color degree    | 26          |
| Chloride%       | 0.06        | Moisture %      | 0.40        | Cr⁶⁺ wet (PPM)  | 1.6         |
| Free CaO%       | 1.83        | L.O.I %         | 3.48        |

According to BS EN 197-1/2011 guidelines [38]; the effect of the cement replacement with firstly SF alone, then both SF with functionalized MWCNTs, and finally both SF with NS in different weight ratios illustrated in table 4 was tested. For studying compressive strengths (2 days, 7 days, and 28 days), bending strengths (2 days, 7 days, and 28 days), the test was applied on 3 prismatic specimens 40 × 40 × 160 mm diameters, with water cement ratio of 0.45, the samples were mechanically mixed then compacted in a mould using a jolting apparatus, then stored for 24 h. in moist atmosphere at 20 ± 1.0 °C and 90% relative humidity. After demolding, samples were stored under water until strength testing, at
the required age, samples were then broken in flexure, for determining bending strength where required, and each half was tested for strength in compression, the physical laboratory room shall be kept at 20 ± 2 °C and 50% relative humidity [42,51].

Table 4. Mix composition of cement mortars with or without SF, SF and functionalized MWCNTs or SF with NS.

| Sample Notation | Cement % | SF Wt. % | Functionalized MWCNTs Wt. % | NS wt.% | Water/Cement Ratio |
|-----------------|----------|----------|-------------------------------|---------|-------------------|
| SF0             | 100.0    | 0.0      | 0.0                           | 0.0     | 0.45              |
| SF2             | 98.0     | 2.0      | 0.0                           | 0.0     | 0.45              |
| SF4             | 96.0     | 4.0      | 0.0                           | 0.0     | 0.45              |
| SF6             | 94.0     | 6.0      | 0.0                           | 0.0     | 0.45              |
| SF8             | 92.0     | 8.0      | 0.0                           | 0.0     | 0.45              |
| SF10            | 90.0     | 10.0     | 0.0                           | 0.0     | 0.45              |
| C0.2SF2         | 97.8     | 2.0      | 0.2                           | 0.0     | 0.45              |
| C0.4SF4         | 95.6     | 4.0      | 0.4                           | 0.0     | 0.45              |
| C0.6SF6         | 93.4     | 6.0      | 0.6                           | 0.0     | 0.45              |
| C0.8SF8         | 91.2     | 8.0      | 0.8                           | 0.0     | 0.45              |
| C0.1SF10        | 89.0     | 10       | 1                             | 0.0     | 0.45              |
| C0.2SF10        | 89.8     | 10       | 0.2                           | 0.0     | 0.45              |
| C0.4SF8         | 91.6     | 8        | 0.4                           | 0.0     | 0.45              |
| C0.6SF4         | 95.2     | 4        | 0.8                           | 0.0     | 0.45              |
| C0.8SF2         | 97.0     | 2        | 1                             | 0.0     | 0.45              |
| NS2SF10         | 88.0     | 10       | 0.0                           | 2       | 0.45              |
| NS4SF6          | 88.0     | 8        | 0.0                           | 4       | 0.45              |
| NS6SF8          | 88.0     | 6        | 0.0                           | 6       | 0.45              |
| NS8SF4          | 88.0     | 4        | 0.0                           | 8       | 0.45              |
| NS10SF2         | 88.0     | 2        | 0.0                           | 10      | 0.45              |
| NS10SF10        | 80.0     | 10       | 0.0                           | 10      | 0.45              |
| NS4SF8          | 84.0     | 8        | 0.0                           | 8       | 0.45              |
| NS6SF4          | 92.0     | 4        | 0.0                           | 4       | 0.45              |
| NS8SF2          | 96.0     | 2        | 0.0                           | 2       | 0.45              |

Standard water required for optimal consistency and setting times were tested as per EN 196-3:2005 [43], mixed cement samples total weight was 500 gm ± 1 gm, the required water was measured, then each sample was mechanically mixed with standard on and off times then moulds were filled determining water required for optimal consistency, and setting times according to the standard procedures using Vicate apparatus [43].

3. Results and discussion

3.1. Single effect of SF on physico-mechanical properties of CMs

3.1.1. Compressive strength. The compressive strength values of CMs containing 2, 4, 6, 8, 10 wt., % of SF cured at 2, 7, and 28 days are reported in figure 13. The compressive strength of CMs increased
with increasing the levels of replacement of SF. Generally, the compressive strengths at 2, 7, and 28 days increased gradually by increasing SF ratio from 2 to 6 Wt.%. A maximum increase up to 9, 2, and 27% was observed in the 2, 7, and 28 days, respectively in the levels containing 6 Wt.%, % of SF. The highest levels of replacement at 8 and 10 Wt.,% showed a gradual decrement in compressive strengths at all ages of hydration. This is due to positive impact of amorphous silica in NS which consuming \( \text{Ca(OH)}_2 \) and increasing CSH which responsible for binding capacity. The additional formation of hydrated calcium silicate (C-S-H) led to more densification in microstructure [44].

![Figure 13. Compressive strength of CMs containing 2, 4, 6, 8, 10 wt. % of SF cured at 2, 7, and 28 days.](image)

### 3.1.2. Bending strength

The bending moment results of CMs containing 2, 4, 6, 8, 10 wt., % of SF cured at 2, 7, and 28 days are showed in figure14. Clearly, the bending strength values increased with increasing SF up 6 Wt., % then decreasing up to 10 Wt., % of SF replacement. The bending strengths at 2, 7, and 28 days of curing gradually increased by increasing SF from 2 to 6 Wt., %. A maximum increment up to 4, 7, and 11 % was observed in the 2, 7, and 28 days, respectively in the samples containing 6 Wt., % of SF.

In general, this increment in bending strength may be due to that, pozzolanic activity of SF with the smallest particle size relative to the size of cement grain. The smallest particle size of silica fume (in range from 50 nm to 150 nm) was found to act as a physical barrier [45]. These results of bending strengths confirmed the pervious results of compressive strength.

### 3.1.3. Water for standard consistence for complete hydration

Water absorption of CMs with or without SF at 2, 7, and 28 days of curing showed in figure 15. The replacement of CMs with SF (2, 4, 6, 8, 10 Wt., %) showed an increment in water consumption for standard consistence (WC) for complete hydration. The water consistency of CMs which containing 10 Wt., % of SF illustrated the highest values. On the other side CMs which containing 6 Wt., % of SF showed decrement in WC comparing to other mixes containing SF. This is attributed to the pozzolanic reactivity of SF and particle size of silica fume (in range from 50 nm to 150 nm)[45].
3.1.4. Initial and final setting times. Both initial setting time (IST) and final setting time (FST) were reported in figure 16. The initial setting time decreased with increasing the replacement levels of SF. On the other side, the final setting time increased with decrement of SF ratios. This is mainly due to impact of amorphous SF which accelerated the hydration reactions in cement matrix. The acceleration of cement provided nucleation sites for Ca(OH)2 within minutes after reaction commences, and also by reacting with Ca2+ ions. The reduction of Ca2+ ion affected the nature of hydration products [46].

3.2. Combined effect of Silica fumes and functionalized MWCNTs on physico-mechanical properties of CMs

3.2.1. Compressive strength. The compressive strength results of CMs containing 2, 4, 6, 8, 10 Wt., % of SF and 0.2, 0.4, 0.6, 0.8, 1.0 Wt., % of functionalized MWCNTs % cured at 2, 7, and 28 days of hydration are plotted in figure 17. A gradually increment in 2, 7, and 28 days compressive strengths were observed by increasing replacement levels of both SF and functionalized MWCNTs. Maximum increasing was observed at (C0.8SF8) which containing 0.8 Wt.,% functionalized MWCNTs and 8 Wt., % SF at early ages of hydration. The compressive strength increased by 15 and 12 % of control sample strength. Notably, The compressive strength of (C0.4SF8) which containing 0.4 W% functionalized MWCNTs and 8 W% SF at 28 days of curing showed increment by 36 %. This is due to duel effect of SF with pozzolanic activity and bridging effect of MWCNTs.
3.2.2. Bending strength. The bending strength results of CMs containing 2, 4, 6, 8, 10 Wt., % of SF and 0.2, 0.4, 0.6, 0.8, 1.0 Wt., % of functionalized MWCNTs % cured at 2, 7, and 28 days of hydration are showed in figure 18. A gradually increment in the bending strength was observed upon increasing the replacement levels of both of them. The maximum value in bending strength was observed at the samples which containing 0.4 Wt.,% of MWCNTs and 4 Wt.,% of SF at early ages of hydration. The bending strength increased by 8 and 11 % at 2 and 7 days, respectively. On other side, at later ages of hydration, the bending strength recorded increment by 17 % at the mix which containing optimum ratio (0.6 Wt., % functionalized MWCNTs and 6 Wt.,% SF).
Figure 18. The bending moment of CMs contains Functionalized MWCNTs and SF with different ratios at 2, 7, and 28 days.

3.2.3. Water for standard consistence for complete hydration. The water consistence of CMs with or without both SF and Functionalized MWCNTs together at 2, 7, and 28 days of hydration showed in figure 19. Obviously, gradually increment in water for standard consistence was observed with high volume SF (10 Wt., %) and low content Functionalized MWCNTs. The (C0.1SF10-mix) showed the highest value in water absorption. This is due to the fact that; the finer spherical particles surface area demands more hydration to attain the required cement properties [47].

Figure 19. Water for standard consistence of cement paste containing Functionalized MWCNTs and SF at 28 days of curing.

3.2.4. Initial and final setting times. Both Initial setting time (IST) and final setting time (FST) were showed graphically in figure 20. IST and FST decreased followed by increasing the content of Functionalized MWCNTs and SF together. All CMs which contained both SF and Functionalized MWCNTs showed the shortest IST and FST comparing to CMs without of them. The mix (C0.2SF10) showed shorter setting times than that the same mixes containing Functionalized MWCNTs and SF. This is due to effect of finer particles of SF and high surface area.
3.3. Duel effect of Silica fumes and Nano silica on physico-mechanical properties of CMs

3.3.1. Compressive strength. The compressive strength results of CMs containing 2, 4, 6, 8, 10 Wt., % of SF and the same values of NS together cured at 2, 7, and 28 days of hydration are reported in figure 21. Notably, at early ages of hydration, the NS8SF4 sample which containing (8 Wt., % NS and 4 Wt.,% SF) showed marginally increasing in compressive strength than other mixes by 8%. The highest increment in 7 and 28 days compressive strengths was observed in case of (NS8SF8) that contained 8 Wt., % NS and 8 Wt., % SF, which increased by 9 and 28 %, respectively. This is due to combined effect of NS and SF which improved physical and mechanical properties of cementations composites. NS consumed Ca(OH)2 and formed additional amount of CSH with high binding capacity.

3.3.2. Bending strength. The bending moment results of CMs containing 2, 4, 6, 8, 10 Wt., % of SF and the same values of NS together cured at 2, 7, and 28 days of hydration were illustrated in figure 22. Minor effect was observed for bending strength (2, 7, and 28 days) of CMs containing both NS and SF with different ratios. At early ages (2 and 7 days) of hydration, the NS4SF8-mix showed the highest bending strength but other mixes decreased by 17 % and 12% in case of NS10SF2- mix. Finally, the bending strength of NS8SF8 –mix showed the highest bending strength at 28days.

3.3.3. Initial and final setting times. Both Initial setting time (IST) and final setting time (FST) of CMs with or without SF and NS together were showed graphically in figure 24. Generally, the decrement in IST and FST was observed by increasing the replacement levels of SF and NS together. The (NS10SF10-Mix) showed the shortest setting times comparing to other mixes. This is due to the high surface area for both of them. Amorphous SF and NS accelerated the hydration reactions in cement matrix especially with high levels of replacement.
**Figure 21.** Compressive strength of cement mortars containing NS and SF with different ratios at 2, 7, and 28 days.

**Figure 22.** The bending moment of cement mortar containing NS and SF with different ratios at 2, 7, and 28 days.

3.3.4. *Water for standard consistence for complete hydration.* Water consistency of CMs with or without SF and NS at 2, 7, and 28 days of curing was presented in figure 23. Clearly, the SF and NS content replaced together with high levels, the Water for standard consistence for complete hydration increased. The sample which didn’t contain SF and NS showed the lowest water absorption. NS10SF10- Mix showed the highest value of water absorption. This is due to high surface area and fine particles of NS and SF which required to absorbed additional water.
Figure 23. Water for standard consistence of plain CEM I (42.5N) and mixtures containing both NS and SF in different ratios.

Figure 24. Initial and final setting times (min) of plain CEM I (42.5N) and mixtures containing both NS and SF in different ratios.
3.4. Microstructure of CMs

The SEM-morphology of cement pastes with or without SF singly, cement paste with mixture of SF and Functionalized MWCNTs and cement paste with mixture of SF and NS illustrated in figure 25. The SEM-morphology of cement paste containing SF (MCSF) showed the rods of CSH which formed due to amorphous silica of SF comparing to control sample (MC0) due to normal hydration of cement. The MCSF-sample showed high microstructure compared to the blank sample due to filling effect of SF. On the other side, the cement paste with mixture of SF and Functionalized MWCNTs (MCSF-MWCNT-mix) showed the bridging effect of functionalized MWCNTs and effect of spherical amorphous silica in SF. This MCSF-MWCNT-mix showed the dual effect of crack bridging with MWCNTs or inters cracks filling with SF. This combined effect showed the densification in microstructure and reflect the good results of compressive strength and bending moment. This sample reported the highest compact comparing to control sample. Clearly, the cement paste with SF and NS together (MCSF-NS-mix) showed the additional CSH with more compact in microstructure. This reported the duel effect of nano-spheres (NS) and amorphous silica (SF) which increased the densification of microstructure. By comparing with control sample, MCSF-NS-mix showed denser in micro-porous structure.

![Figure 25. SEM-photos of cement pastes with SF singly, cement paste with mixture of SF and Functionalized MWCNTs and cement paste with mixture of SF and NS.](image)

4. Conclusion

Performance of CMs incorporated of silica fumes, purified functionalized MWCNTs and nanosilica was studied. Generally, increment of compressive and bending strengths (due to the fact that MWCNTs bridge the cracks) was observed. No significant effect on water consumed for optimum consistence was observed, while initial and final setting times were generally decreased. This effect may be due to the fact that MWCNTs are highly dispersive in water so increase mixing homogeneity. Meanwhile the replacement of cement composites with NS and SF showed increasing in physico-mechanical properties such as compressive, bending strengths, and water consistency due to the finer spherical particles of NS
and surface area that demanded more hydration to attain the required cement properties but setting times were significantly decreased. The combination between MWCNT and SF showed the good duel effect on mechanical properties more than the impact of NS and SF. This combination between MWCNT and SF led to enhance the physico-mechanical properties of CMs. The results of compressive, bending strengths, water consistency and setting times were confirmed by SEM-morphology which showed more compact in microstructure. This investigation, presented eco-friendly technique to prepare the nanoparticles to enhance the mechanical properties of CMs.

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