Influence of functionalized MWCNT on microstructure and mechanical properties of cement paste

MOHAMMAD ALI MOUSAVI* and ALI BAHARI

Department of Physics, University of Mazandaran, Babolsar, Iran
e-mail: ali.mousavi@stu.umz.ac.ir; a.bahari@umz.ac.ir

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Abstract. Today, studies on nanotechnology applications in the construction industry are looking for a solution to reduce the use of cement and consequently to reduce the emission of pollutants in the environment. In this regard, the effect of different percentages of the functionalized multi-walled carbon nanotubes with carboxylic groups (MWCNT) on the modification of mechanical and microstructural properties of hardened cement paste was investigated. The addition ratios of Portland cement with the same weight of MWCNT-COOHs were 0, 0.025, 0.05, 0.1, and 0.2 weight percent (wt%). Moreover, the mechanical and microstructural properties of the hardened cement paste were investigated by the use of Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), X-powder, scanning electron microscope (SEM) and atomic force microscope (AFM) techniques. The results show that replacement of cement with 0.05 wt% of the functionalized carbon nanotube, as the optimal amount, can be considered both for improving mechanical and microstructural properties.

Keywords. Nanomaterials; micro-crack; micro-pores; Portland cement; multi-walled carbon nanotubes.

1. Introduction

The process of cement production is very complex and is associated with the consumption of fossil fuels; thus, reducing the amount of cement in concrete indirectly reduces the emission of pollutants. It has been shown that the replacement of cement with 4% nanoparticles such as silica and iron oxides increases the physical and chemical properties of concrete along with saving of cement consumption [1]. Some researchers have tried to increase the properties of materials used in the construction industry, including cement [2–5] and concrete [6–10] by the use of nanotechnology. In the recent years, nanotechnology has provided a chance to use nanoscale materials such as nanoparticles [11–14], nanotubes and nanofibers with specific surface areas in the construction industry. The performed studies [15–22] show that some nanoparticles including nanosilica can improve the properties of some construction materials. Moreover, the emergence of carbon nanotubes has provided the possibility for the improvement of the volume stability of cement-based materials [23]. In some studies, carbon nanotubes have been synthesized through chemical vapor deposition from polyethylene [24]. In some other studies, CNTs were synthesized on Portland cement by the use of CVD method along with Fe catalyst, and the effects of different parameters including

temperature, reaction time, and the amount of catalyst involved in the reaction were assessed. Results showed a growth starting at 700–800°C for thin multi-walled nanotubes and at 850–900°C for multi-walled carbon nanotubes with larger diameters. If the amount of added catalyst violates 2.5 wt% in CNTs, the diameter in synthesized carbon nanotubes will increase [25]. Carbon nanotubes increase the hardness of C-S-H and fill the pores [26]. One of the main problems with carbon nanotubes is accessing their uniform distribution in the cement matrix [27]. Ying *et al* studied the effect of carbon nanotubes with 0.05 wt% cement and found that compressive strength in hardened cement increases up to 19% after 28 days, while flexural strength rises up to 25%. They also revealed that porosity and pore size distribution increase [28]. Moreover, electrical resistance and pressure-sensitive properties of carbon nanotubes impregnated in a solution of sulfuric acid and lack of hydrogen nitrate were studied [29]. Yet another study was carried out on microstructural properties of reinforced cement paste with MWCNT and nano-sized Fe needles using SEM and AFM. It demonstrated that, despite the strong connection between needles and nanotubes, there is a weak link between carbon nanotubes and the cement matrix [30]. To simultaneously access a uniform distribution for carbon nanotubes in cement matrix, the ultrasonic method was employed in the presence of sodium dodecyl sulfate and polyoxyethylene in different densities. In another study, the relation between the quality of dispersion

*For correspondence

Table 1. Chemical compositions of PC obtained by using XRF analysis (% by weight).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	C ₃ S	C ₂ S	C ₃ A	LOI
PC	21.91	5.05	4.45	62.15	2.27	2.19	0.31	0.63	39.30	34.39	5.85	0.55

PC: Portland cement; LOI: loss on ignition.

rate in CNTs and dispersion time was examined by the ultrasonic method, and also the density of used surfactant was studied by UV-Vis spectroscopy. Two types of nanotubes were utilized in the study: one was a combination of carbon nanotubes with one, two, or multiple walls, and the other was nanotubes doped with nitrogen. The optimal mass ratios of surfactant-CNT were 1:1 and 1:1.5, and the optimal time of dispersion by the use of ultrasonic method was 120 min. Results indicated that there was no major difference between utilizing each type of surfactant for dispersing carbon nanotubes [31]. Experimental research was conducted to determine the optimal mixing dose of CNTs in cement paste in the presence of plasticizer (as a surfactant for MWCNT) through specifying flexural and compressive strength. The best result belonged to a situation in which surfactant weighed 0.008 of cement weight and the dose rate of MWCNT was between 0.1 and 0.3% [32]. In the above study, in order to improve the mechanical, nano-structural and chemical properties of the specimens, as well as to consider environmental aspects, it was tried to add 0, 0.025, 0.05, 0.1, and 0.2 percent of cement with functionalized carbon nanotube in the cement paste. In order to achieve uniform distribution in the cement matrix and suitable bonding of the nanotubes with cement matrix, the carboxyl group was used as a polar impurity in MWCNT as an agent for bonding between the hydrophilic polar cement matrix and non-polar carbon nanotubes in the hydration process. Moreover, ultrasonic bath was used for distribution of MWCNT in water. Then, mechanical properties of the specimens were evaluated according to ASTM standards and through analyzing data, figures and spectra obtained from X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), X-powder, scanning electron microscope (SEM), and atomic force microscope (AFM) techniques, the effect of using nanotubes in cement and its role in modifying the nanostructured properties of cement matrix was investigated.

2. Materials and methods

Type II Portland cement produced in Neka Cement Corporation (Mazandaran, Iran) was employed in the present study complying with ASTM C150, 2004 [33]. Chemical properties of the cement used in quality controlling of the cement company's laboratory were studied and are presented in table 1. Mechanical properties of MWCNT (Produced in Neutrino Co.) applied in the mentioned

Table 2. Physical properties of MWCNT-COOH.

Property	Value
Purity	> 95%
Outside diameter	15–35 nm
Inside diameter	8–5 nm
Length	≈ 50 μm
Color	Black
True density	2.1(g/cm ³)
Electrical conductivity	100 s/cm
Manufacturing method	CVD

project can be observed in table 2. According to the documentation provided by the manufacturer, these materials were produced by the chemical vapor deposition method.

2.1 Preparation of cement paste samples

In this study, Twenty-four series of mixed cement paste including six control samples (CS) as samples without carbon nanotubes (each sample with a specific age included two sizes) and other samples containing MWCNT approximately 0.025, 0.05, 0.1, and 0.2 wt% of Portland cement were used according to table 3. The cement paste samples were prepared according to ASTM C109, 2002 [34] standard with the water to binder (cement + MWCNT) ratio of 0.425. For better dispersion of nanomaterials in cement paste matrix, MWCNT was dispersed in deionized water using a magnetic stirrer before adding cement to make a suspension. After that, cement was added and the mixture was dispersed in water in an ultrasonic bath (Elma, Iran) for 30 min at 25°C for a more uniform dispersion. Then, the mixture was blended by the use of a mechanical blender (TESTING Bluhm & Feuerherdt GmbH, Berlin). The applied mixer for this experiment was in accordance with ASTM C511, 2013 [35] with a planetary motion of 285 rpm for paste. During the test, the laboratory temperature was $20 \pm 2^\circ\text{C}$ and the humidity was above 50%. In this way, our samples were prepared for mechanical experiments. The samples were demolded 24 h after they were cast and then cured in water basin at $23 \pm 2^\circ\text{C}$ for 2, 6, and 27 days.

2.2 Mechanical tests

Mechanical properties of cement paste including compressive and flexural strength of the samples were studied on days 3, 7 and 28. Compressive strength was carried out

Table 3. Mixture designs of cement paste.

Mixture	CNTs (wt.%)	Mix protection		
		Cement (g)	CNTs (g)	Water (cc)
CS	0	600	0	255
SCNT1	0.025	599.85	0.15	255
SCNT2	0.05	599.70	0.3	255
SCNT3	0.1	599.40	0.6	255
SCNT4	0.2	598.80	1.2	255

CS: Control sample.

on samples based on ASTM C109, 2002 [34] standard. For this purpose, 15 cubic specimens ($50 \times 50 \times 50 \text{ mm}^3$) were prepared. Then, flexural strength tests were carried out on samples based on the ASTM C348, 2002 [36] standard. In this regard, 15 prismatic samples ($160 \times 40 \times 40 \text{ mm}^3$) were prepared. The mechanical tests were carried out by cement testing machine (DIGICON, 2100, Swiss) with capacity of 200 kN and a loading speed of 2.4 kN/s for compressive strength and with capacity of 10 kN and a loading speed of 0.5 kN/s for flexural strength.

3. Results and discussions

3.1 Results of mechanical tests

Table 4 shows the results of the mechanical properties of the hardened cement paste including compressive and flexural strengths at different ages with different weight ratios of MWCNT.

3.1a Compressive strength: Figure 1 demonstrates changes in the compressive strength of the samples during 3, 7, and 28 days with different weight ratios of MWCNT. The graph shows that adding MWCNT up to 0.05 wt% of cement increased the compressive strength of the samples significantly. The maximum values of the compressive strength of

the samples were obtained when the replacement ratio of cement with the same weight of MWCNT was 0.05 wt% (SCNT2). In addition, the increase rate of the compressive strength of SCNT2 in comparison with CS equaled approximately 14, 8.7 and 26.6% for 3, 7 and 28 days, respectively.

3.1b Flexural strength: Changes in the flexural strength of the hardened cement paste are depicted in figure 2, detailed with different weight ratios and ages. Similar to the compressive strength, as the age of the sample grew, the flexural strength increased. This is while the flexural strength of the sample was extremely higher in 7 and 28 days than in the early ages. Moreover, the optimal weight percentage for MWCNT was 0.05 wt% and the flexural strength of SCNT2 on days 3, 7, and 28 was nearly 14%, 8%, and 3.2% higher than that of CS, respectively. It was observed that MWCNT had the greatest effect on the flexural strength of the samples on days 3 and 7, which could be due to the reactivity of cement compounds and increased hydration rate in the presence of carbon nanotubes. MWCNT tend to be aggregated and come in accumulation. It can be mentioned that, because of the COOH group and use of ultrasonic bath, the agglomerates were separated and dispersed in a cementitious matrix, thereby helping to improve the mechanical properties of the samples.

3.2 Microstructure analysis

In examining the mechanical test results in the previous section, the sample containing 0.05 wt% of MWCNT was obtained as optimum percentage. Then, for the purpose of studying the effect of MWCNT on the cement microstructure, the samples of the hardened cement paste containing 0.05% of MWCNT at different ages were investigated and the results were compared with the CS results using the following methods.

3.2a XRF analysis: X-ray fluorescence was applied to quantify the elemental composition of different cement powders. In this method, it was determined that which

Table 4. Results of mechanical testes.

Mixture	Compressive strength (MPa)			Flexural strength (MPa)		
	3 days	7 days	28 days	3 days	7 days	28 days
CS	17.65 (± 0.89)	40.29 (± 0.81)	47.06 (± 0.85)	3.74 (± 0.09)	8.30 (± 0.20)	9.45 (± 0.23)
SCNT1	18.50 (± 0.87)	42.40 (± 0.87)	54.40 (± 0.72)	4.20 (± 0.03)	8.70 (± 0.25)	11.62 (± 0.23)
SCNT2	20.11 (± 1.00)	43.80 (± 0.89)	59.56 (± 0.98)	4.94 (± 0.10)	10.80 (± 0.22)	11.82 (± 0.24)
SCNT3	19.53 (± 0.98)	42.00 (± 0.89)	49.26 (± 0.85)	4.64 (± 0.09)	10.30 (± 0.20)	10.79 (± 0.21)
SCNT4	18.26 (± 0.96)	41.40 (± 0.87)	46.46 (± 0.82)	4.46 (± 0.09)	9.10 (± 0.19)	9.87 (± 0.20)

Figure 1. Compressive strength of samples in several days.

Figure 2. Flexural strength of samples in several days.

percentage of the elements in the samples at different ages was found. The results of XRF analysis were recorded by total cement analyzer (model ARL 8680S), as presented in table 5(a)–(c). The phases formed in the hydration process were hydrated at different times. Therefore, the mechanical properties of different ages of the sample can be attributed to the hydration of the phases. By comparing the results of the XRF analysis in table 5 with the results of the mechanical test shown in figures 1 and 2, it was concluded that the increase in the compressive and flexural strengths on days 3 and 7 can be due to an increase in the percentage of the C_3S phase and a decrease in the percentage of the C_2S phase, respectively. For example, the comparison between SCNT2 and CS showed that increased compressive and flexural strengths in 28 days could respectively be

due to an increase in the percentage of the C_2S phase and a decrease in the percentage of the C_3S phase in the SCNT2 sample relative to CS. Thus, it can be concluded that the increase of the C_3S phase improved the mechanical properties at an early age. Moreover, with increasing the age of the sample, the C_2S phase improved its mechanical properties. We can also discuss the relationship between the percentage of the other phases determined in XRF analysis with mechanical and microstructural properties of the samples. So, an increase in the aluminate phase in a cement paste containing MWCNT on the days 3 and 7 compared with control samples shows that the hydration rate increases with the presence of carbon nanotubes. It also increases the durability of cement base products. The comparison of C_4AF phase in samples containing nanomaterials with control sample on days 3 and 7 indicates that this phase has decreased.

3.2b XRD analysis and XRD powder technique: The XRD method can be used to determine phase identification, crystal size measurement, and crystallinity. The phases of the cement paste powder samples, without MWCNT and with 0.05% of it, were analyzed qualitatively and quantitatively in 3 and 28 days by XRPD [W: 1200, 35: KV, 30: mA] with a tube FK 60-04, cobalt anode, and linear focus, and the data were collected as follows: Time per step: 1 sec; angular range: 5° – 80° ; total acquisition time: 01:02 h; degrees/min: $\frac{1}{2}$. The XRD patterns of cement paste without MWCNT and cement paste mixed with MWCNT are shown in figure 3 at 3 and 28 days. Calcium hydroxide $Ca(OH)_2$ phase peaks can be seen at 21° , 40° , 55.85° and 59° and have a hexagonal network with Miller index ($a = 3.59$, $b = 3.59$, $C = 4.89$; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$).

Peak intensity was compared in the powder samples of cement paste without nanotube or with 0.05% of it on the days 3 and 28 in a qualitative analysis. As can be observed from figure 3, the intensity of the peaks at 20.93° , 39.79° , 55.3° and 59.88° for the samples containing 0.05 wt% of MWCNT in 28 days was less than those of the controls due to the decrease of $Ca(OH)_2$ amount or amorphous structure of the sample. These results show the improvement of the nano-structural properties of the SCNT2 sample and confirm the increased mechanical strength studied in the previous section. As shown in figure 3, in comparison with the control sample pattern, the C_3S peak intensity in the sample increased on the day 3 while decreased on day 28, which is consistent with the XRF analysis results. Moreover, in comparison with the control sample pattern, the C_2S peak intensity increased in the sample on the day 28, confirming the results of the XRF analysis.

The data were quantitatively analyzed by the Scherrer method using the X-Powder software. In order to measure the approximate sizes of the crystal phases, the width of the peak was measured at half the maximum intensity (FWHM) and the highest-intensity peak was chosen.

Table 5. XRF analysis of samples: (a) 3 days; (b) 7 days; (c) 28 days.

Chemical composition Compound	PC	PC + 0.025%CNT	PC + 0.05%CNT Content (%)	PC + 0.1%CNT	PC + 0.2%CNT
<i>(a)</i>					
SiO ₂	20.91	20.89	20.89	20.8	20.94
Al ₂ O ₃	4.74	4.74	4.74	4.73	4.75
Fe ₂ O ₃	3.37	3.34	3.3	3.32	3.31
CaO	61.04	60.97	60.67	60.47	61.03
SO ₃	1.57	1.62	1.64	1.62	1.68
K ₂ O	0.55	0.54	0.54	0.58	0.49
LSF	90.35	90.31	89.86	89.91	90.16
SM	2.58	2.59	2.6	2.58	2.6
AM	1.4	1.42	1.43	1.43	1.43
C ₃ S	48.45	48.23	47.01	46.94	47.92
C ₂ S	23.43	23.52	24.45	24.25	23.9
C ₃ A	6.85	6.91	6.98	6.93	6.96
C ₄ AF	10.26	10.16	10.06	10.1	10.08
Total	93.6	93.53	93.22	92.95	93.64
Chemical composition Compound	PC	PC + 0.025%CNT	PC + 0.05%CNT Content (%)	PC + 0.1%CNT	PC + 0.2%CNT
<i>(b)</i>					
SiO ₂	20.69	20.55	20.55	20.6	20.7
Al ₂ O ₃	4.72	4.68	4.69	4.69	4.71
Fe ₂ O ₃	3.27	3.19	3.2	3.2	3.28
CaO	60.09	59.53	59.57	59.57	60.27
SO ₃	1.39	1.47	1.34	1.34	1.49
K ₂ O	0.5	0.54	0.54	0.54	0.56
LSF	90.09	89.92	89.98	89.98	90.19
SM	2.59	2.61	2.61	2.61	2.59
AM	1.44	1.47	1.46	1.46	1.43
C ₃ S	47.1	46.3	46.45	46.45	47.44
C ₂ S	23.8	24.02	24.31	23.91	23.59
C ₃ S	6.97	7.01	7.01	7.01	6.92
C ₄ AF	9.96	9.72	9.74	9.74	9.99
Total	92.09	91.27	91.31	91.31	92.45
Chemical composition Compound	PC	PC + 0.025%CNT	PC + 0.05%CNT Content (%)	PC + 0.1%CNT	PC + 0.2%CNT
<i>(c)</i>					
SiO ₂	20.79	20.84	20.86	20.79	20.9
Al ₂ O ₃	4.74	4.75	4.73	4.74	4.7
Fe ₂ O ₃	3.28	3.33	3.3	3.27	3.31
CaO	6.43	61	60.8	60.4	60.88
SO ₃	1.52	1.55	1.49	1.5	1.58
K ₂ O	0.49	0.51	0.53	0.53	0.5
LSF	90.03	90.62	90.35	90.01	90.17
SM	2.59	2.58	2.6	2.6	2.59
AM	1.44	1.43	1.44	1.45	1.44
C ₃ S	47.18	48.9	48.25	47.11	47.83
C ₂ S	24.03	22.88	23.42	24.1	23.87
C ₃ A	7	6.97	6.96	7.03	7.01
C ₄ AF	9.99	10.12	10.03	10.06	10.07
Total	92.68	93.42	93.14	92.66	93.35

Figure 3. XRD patterns of CS and reinforced samples at the ages of 3 and 28 days.

Based on Scherrer's model according to Eq. (1) [37]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

In which D is the crystal size, β is the peak width at half the maximum intensity, θ is the Bragg angle related to the peak, and γ is the X-ray wavelength. Based on the equation, as the peak width increased, the crystal size decreased as a result of the addition of functionalized carbon nanotubes in cement paste. As it is clear in figure 4, the graphs drawn by X-Powder suggest that the hardened cement paste containing carbon nanotube on the day 28 (a) had smaller nanocrystallines than the cement paste containing carbon nanotube on the day 3 (b). Further, the size of nanocrystallines in the cement composites without carbon nanotube (c) was much larger. Due to the formation of smaller nanocrystals with the presence of MWCNT, compared with the control sample, they provide more reactive surface areas that can provide a more nucleation site for the formation of calcium silicate hydrates which leads to a denser microstructure and the mechanical properties of cement-based products are enhanced.

3.2c FTIR properties: To determine the quantitative and qualitative properties of organic compounds containing carbon nanotubes, types of the functional group and the bonds in their molecules can be determined using the FTIR spectrophotometric method. Figure 5 illustrates the chemical bonds between the cement paste sample with 0.05% carbon nanotube and CS on the days 3, 7 and 28 in a range of 400–4000 cm^{-1} . Table 6 represents the functional groups in the cement paste powder for a specific wavenumber. Using these groups, structural differences in the hydration behavior for CS and the samples containing 0.05% of carbon nanotube can be identified on the days 3, 7 and 28. As identified in table 6 and figure 5, the vibration mode showed the functional group of $\text{Ca}(\text{OH})_2$ in the wavenumber of 3457 cm^{-1} . The peak intensity in the sample with MWCNT decreased during 28 days. The effects of adding carbon nanotube to the samples on the peak intensity were consistent with the results of the XRD analysis.

The wavenumber 3467 cm^{-1} in the samples showed that the stretching vibration of water molecules absorbed with C-S-H gel surfaces was produced through the hydration process. Due to decrease in the peak intensity by adding MWCNT, it can be concluded that hydration took place

Figure 4. Size of nanocrystalline for (a) CS, (b) reinforced samples at 3 days, (c) at 28 days, calculated with the Scherrer equation and X-powder technique.

with further delay, and it is clear that an increase in the age of the hardened cement paste caused a significant decrease in the peak intensity. The flexural vibration mode in water molecules was obvious by the wavenumber 1647 cm^{-1} in the cement paste samples and the molecules participated in C-S-H gel production. The peak intensity decreased when MWCNT were added. This decrease showed the lower production of C-S-H gel in the 3 and 7 days; when the samples became older, the peak almost disappeared. The wavenumber 1429 cm^{-1} was the stretching vibration mode of the functional group CO_3 related to CO_2 absorption during the hydration process. Due to the decrease in the peak intensity, it is suggested that the sample strengthened by

MWCNT absorbed fewer environmental gases during the hydration process. In CS, the vibration of the functional groups V_4 of SiO and AlO_6 as well as V_4 of CO_3 was observed in the wave numbers 463 cm^{-1} , 714 cm^{-1} , and 850 cm^{-1} . However, the vibration was very weak in the cement paste samples on days 3 and 7, and it disappeared in the samples containing CNT on the day 28. This showed that adding carbon nanotube caused a decrease and elimination in the functional groups. The results of FTIR analysis on cement paste with and without functionalized carbon nanotubes indicate that stronger bonding and better absorptive reactions will be formed by replacing nanotubes with 0.05 wt% of cement in cement paste samples in the hydration process. The stronger bonding can be an indication for improvement in chemical, mechanical, and microstructural properties of samples. Therefore, the results of FTIR analysis are in good compatibility with the findings of mechanical tests.

3.2d SEM analysis: To investigate the microstructures and morphology of the samples, scanning electron microscopy was used. The reason for the use of this test was to evaluate how MWCNT were placed inside cement matrix and dispersed nanomaterials. For this purpose, after mechanical tests, the broken specimens were pulverized and then imaged by a scanning electron microscope (SEM). The microstructures of the original phases produced through the CS hydration at different ages and the specimens produced by adding 0.05% of the nanotubes at different ages are illustrated in the SEM images in figure 6(a)–(d). As figure 6(b) suggests, MWCNT were relatively uniformly dispersed within the cementitious matrix and the $\text{Ca}(\text{OH})_2$ crystals shaped as multi-dimensional crystals in the nanometer were produced at an early age. Moreover, it was also demonstrated that a number of MWCNT agglomerates were found at scattered points that might have established physical bonding with the cement matrix. Comparison of figure 6(c) and (d) show that matrix structures hiding under carbon nanotubes occurred in 7 days. According to figure 6(d), carbon nanotubes made bridges on the micro-cracks and micro-pores in the cement matrix and caused a decrease in the production of calcium hydroxide functional groups. Moreover, bridging MWCNT on the nano-pores and filling the micro-pores led to an increase in the mechanical properties of cement paste reinforced with nanotubes, which was consistent with the results of the mechanical tests. The filling of the pores and production of extremely small nanocrystalline can be observed by comparing SEM images related to the 28-day-old cement composite with or without nanotube as shown in figures 6(e) and (f). By comparing the compressive strength in the two samples, a full consistency can be observed between the results of these studies. However, the production of C-S-H gel structure and C-H crystals was obvious in the 28-day-old samples containing MWCNT. The C-S-H, such as coatings around carbon nanotubes, formed a condensed matrix. Therefore, in a general view of

Figure 5. FTIR spectra of CS and reinforced samples at the ages of 3, 7, and 28 days.

Table 6. Wavenumbers and functional groups in FTIR spectra of PC.

Wave number (cm ⁻¹)	Functional groups	Reference
448–463	ν_4 of SiO	[38, 39]
500	SiO ₆ bend	[40–43]
656–658	ν_4 of SiO ₄	[44–47]
714	ν_4 of CO ₃	[39]
850	AlO ₆	[39]
920–940	SiO ₄	[44, 45, 48, 49]
1100–1200	ν_3 of SO ₄	[44, 46–48, 50]
1400–1500	CO ₃	[40, 43, 46, 51]
1640–1650	ν_2 of H ₂ O	[48, 52]
1795–1796	SiO ₄	[48, 52]
2983–2984	CaCO ₃	[40, 51]
3457	$\nu_1 + \nu_3$ of H ₂ O	[42, 43, 47, 52–54]
3641–3644	Ca(OH) ₂	[52]

the SEM images, it can be concluded that MWCNT using the physical bond with the cement network and the chemical bond between the COOH impurity agent and hydration products can significantly prevent the spread and release of cracks and play the role of joint filler. This can be attributed to the fact that there was a very good interaction between hydration products and dispersed MWCNT, which resulted in a denser microstructure production as compared to unreinforced cement paste.

3.2e AFM technique: In order to determine the topography of sample surfaces and to detect various physical aspects of the surfaces, atomic force microscope (AFM), was used. First, samples were dried for 24 h at 110°C. Then small pieces of material were manually glued onto AFM sample holder and slightly polished in dry conditions (40–60% relative humidity). The reason for this test is to evaluate the surface in CS and the samples with 0.05% of MWCNT were compared by the use of Nanosurf software on days 3 and 28 in the forms of 2-D view and 3-D view (figure 7). The structures Ca₃SiO₄ and Ca₂SiO₄ were observed in sample surface which was the result of adding carbon nanotube. Moreover, surface roughness for the cement paste without carbon nanotube, the sample with 3-day-old carbon nanotube, the one with 28-day-old carbon nanotube equaled 205 nm, 138 nm, and 80.9 nm, respectively. Furthermore, as shown in AFM topography spectra demonstrated, the samples containing MWCNT have less surface roughness and fewer cracks.

In order to determine the topography of the sample surfaces and to detect various physical aspects of the surfaces, atomic force microscope (AFM) was used. The reason for the use of this test was to evaluate the surface in CS; the sample with 0.05% of MWCNT was compared by the use of Nanosurf software in the forms of 1-D, 2-D and 3-D view (figure 7). The structures Ca₃SiO₄ and Ca₂SiO₄ were observed in the sample surface as the result of adding

Figure 6. SEM images of (a) CS at 3 days, (b) reinforced samples at 3 days, (c) CS at 7 days, (d) reinforced samples at 7 days, (e) CS at 28 days, and (f) reinforced samples at 28 days.

carbon nanotube. Moreover, CS has an uneven surface with more pores, and the surface is smooth in small portions, and in most areas it has a rough surface. Adding the MWCNT-COOH in the sample caused topographic changes on the sample surface. The surface morphology of reinforced

cement paste has less roughness. The roughness is described as a statistical characteristic of a surface. Table 7 shows the roughness parameters which were determined by means of Nanosurf method. The S_a , S_m and S_q are the roughness average, mean value of the roughness and the

Figure 7. Microscopy and surface morphology analysis of (a) CS at 28 days, (b) reinforced samples at 2 days, and (c) reinforced samples at 28 days.

Table 7. Surface roughness factors of samples obtained with Nanosurf software.

Mixture	Roughness (nm)				
	Area (pm ²)	S _a	S _m	S _q	S _y
CS	23.19	2.24	0.431	3.22	115.20
SCNT2 (2 days)	23.05	1.53	0.296	2.80	63.17
SCNT2 (28 days)	22.98	0.48	0.203	1.33	20.49

root mean square of the roughness respectively, which can be calculated according to Eqs. (2) to (4).

$$S_a = \frac{1}{N} \sum_{l=0}^{N-1} |z(x_l)| \quad (2)$$

$$S_m = \frac{1}{N} \sum_{l=0}^{N-1} z(x_l) \quad (3)$$

$$S_q = \sqrt{\frac{1}{N} \sum_{l=0}^{N-1} (z(x_l))^2} \quad (4)$$

In which $z(x_l)$ is the roughness. S_y as the peak-valley height is the difference between the meanings of the largest peak and valley. It can be concluded that the decrease in the S_y parameter in the sample shows less roughness. The reinforced samples compared to CS, have less roughness and their surfaces are softer. Furthermore, reinforced sample in 28 days is softer and has fewer cracks than reinforced sample in 3 days. Considering the fact that reduction of surface roughness can lead to increase of flexural strength, the AFM analysis results are compatible with the mechanical test results.

4. Conclusion

In the present experimental study, the effect of different weight percentages of MWCNT on the mechanical and microstructural characteristics of cement paste was investigated. The XRF analysis expressed the variations in chemical phases in the hydration process. The X-ray analysis and X-Powder technique determined the phases and their relative proportions by the intensity of the diffraction peaks and the size of nanocrystalline. The FTIR analysis determined the chemical structures. The SEM analysis described an overview of surface texture; and the AFM analysis provided a detailed image of the specimens and the microstructure of their pores. The major results of the study are as follows:

- The results of XRD and FTIR analysis showed that better chemical reaction in the hydration process occurred in the presence of MWCNT, leading to enhancement of the cement matrix.

- The results of XRF analysis indicated that nanomaterial presence accelerates the hydration degree in cementitious matrix.
- The inhomogeneous surface of the sample containing carbon nanotube decreased in comparison with the control sample.
- As AFM images and Nanosurf analysis showed, the reinforced cement paste samples have less surface roughness and fewer cracks compared to the CS sample. Furthermore, the reinforced cement paste in 28 days has less surface roughness than the other one in 3 days.
- MWCNT formed a denser matrix by filling the micropores and C-S-H gel porosity. Therefore, they significantly prevented the spread and release of microcracks and functioned as joint filler.
- Generally, mechanical characteristics of cement paste improved by replacing 0.05 wt% of Portland cement with MWCNT, due to enhancement of cement matrix microstructure.
- Functionalized MWCNT had the highest efficiency in increasing the flexural strength of the samples at the early ages (3 days) as well as increasing the compressive strength of the samples at the final ages (28 days).
- The increase in the strength of the samples containing MWCNT-COOH at the early ages (3 days) can be related to bonding between the hydrophilic polar cement matrix and non-polar carbon nanotubes in the hydration process.
- Adding 0.05 wt% of MWCNT resulted in the highest increase (27%) in the compressive strength of the 28-day sample and the highest increase (14%) in the flexural strength of the 3-day sample.
- The use of MWCNT with a percentage greater than 0.05 caused agglomeration due to the lack of uniformity of distribution which reduced the mechanical properties and negatively affected the microstructural properties of the samples.

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