

Effect of Using Hybrid Nano-Particles on Physical and Mechanical Properties of Cement Mortar

Ahmed H. Abd El-Raheem^a, Sohir Negm^b, Ahmed M.Tahwia^c, Basma A. Abd El-Rahman^{d*}

^aProfessor in Faculty of Engineering, Mansoura University, Structural Engineering Department, Egypt

^bProfessor in Faculty of Engineering (Shoubra), Benha University, Math and Physics Department, Cairo, Egypt

^cAssistant Professor in Faculty of Engineering, Mansoura University, Structural Engineering Department, Egypt

^dPost graduate Student in Faculty of Engineering, Mansoura University, Structural Engineering Department, Egypt

^aEmail: ahmed_abd_el_raheem@yahoo.com

^bEmail: drnegm@hotmail.com

^cEmail: atahwia@yahoo.com

Abstract

This research evaluates the addition of graphene sheets and hybrid nano-materials (graphene with different nano-materials like nano-silica or nano-clay) on compressive strength, flexural strength and thermal conductivity of cement mortar. Graphene sheets were added in three percentages (0.04%, 0.05%, and 0.06%) and (0.03%, 0.04%, and 0.05%) graphene sheets with 1% nano-silica or with 5% nano-clay by weight of cementitious materials. For all specimens, w/c ratio 0.4 was applied. Scanning Electron Microscope and thermal conductivity tests were also performed on the optimum specimens at age 28 days. Results indicated that the optimum dose of graphene sheets was 0.05% by weight where the compressive strength, the flexural strength were improved by 35.66% and 33.33% respectively, and low thermal conductivity by 6.36% at age 28 days. No significant increase in compressive and flexural strength on adding hybrid nano-materials (graphene sheets with 1% nano-silica) to mortar. Also reduction effect in compressive and flexural strengths was achieved on adding hybrid nano-materials (graphene sheets with 5% nano-clay) to mortar. High thermal conductivity was obtained at age 28 days with respect to control ones when hybrid nano-materials were added to cement mortar.

Keywords: Graphene sheets; Nano-silica; Nano-clay; Compressive strength; Flexural strength; Thermal conductivity.

* Corresponding author.

1. Introduction

In recent years, carbon (C) based materials have drawn attention and were incorporated in the cement matrix for strengthening. Among the family of carbon-based materials, 1D carbon nano-tubes and 2D graphene seem promising as viable alternatives to the conventional nano-materials used in cement due to the versatile chemistry of carbon and its outstanding mechanical properties due to strong C-C bonds [1]. Graphene sheet – one-atom-thick two-dimensional (2D) layers of SP²-bonded carbon (C) that illustrated in figure 1 is the thinnest known material by Novoselov, and his colleagues because of unique electrical and mechanical properties such as high electron mobility and stiffness [2]. It is first introduced by Mouras, and his colleagues. (1987) as the two-dimensional (2D) from graphite [3]. Graphite is composed of a series of superimposed layers of a hexagonal network of carbon atoms, in which each atom is bound by three neighboring carbon atoms in a planar network. Separating these layers into a monolayer around one nanometer thick makes it possible to obtain graphene foils. This allows unique electronic, magnetic, optical and mechanical properties to appear [4]. Single-wall CNTs (SWCNTs), multi-wall CNTs (MWCNTs) [5] as illustrated in figures (2a - 2b) can be represented as a graphene sheets rolled in to a cylinder with a specific alignment of hexagonal rings and hemi fullerenes attached to the tips [6] with very large aspect ratios (of 1000 or more) and very high surface areas [7].

Furthermore, it has been noted that enriched by graphene nano-material merely 0.01 % to 1 % of the weight of the Portland cement, the concrete compressive strength could be improved from 5% to 40%, depending on the particle dimension of the additive materials and the different treatment methods that have been used in the experiments [8]. Very limited work has been reported on the behavior of cement mixed with graphene sheets. The addition of small amounts of graphene sheets to cement may cause an increase in the composite material toughness and tensile, flexural, and impact strength because of unique electrical and mechanical properties such as electron mobility and stiffness [9]. Graphene oxide (GO) nano-sheets can regulate the cement hydration reaction crystals shapes with a uniform distribution in the cement paste, resulting in a clear increase in the mechanical strength, especially flexural strength. Graphene-oxide (GO) nano-sheets may reduce the brittleness and enhance toughness, tensile and flexural strength of the hydrated cement composite [10].

Ahmadreza Sedaghat and his colleagues (2014), showed that graphene-oxide (GO) nano sheets may reduce the brittleness and enhance toughness, tensile and flexural strength of the hydrated cement composite. GO can regulate cement hydration and distinctly affect the mechanical properties of hydrated cement composite such as increasing strength, preventing cracking and reducing porosity [11]. Pan, and his colleagues (2015), tested the effect of graphene oxide (GO), or functionalized graphene on the strength of Portland cement paste. The study concluded that adding 0.05 wt% GO increased the compressive strength by at least 15% and the flexural strength by at least 41%. It showed that GO served as a barrier to crack propagation, stopping cracks at the nano-scale [12]. Another experiment published by the American Society of Civil Engineers, concluded that the introduction of 0.03% graphene oxide by weight cement reduced the number of pores in the material and increase the strength by over 40% [13]. Lv and his colleagues (2013), studied the effect of graphene oxide on the strength of mortar mixes, and concluded that the addition of 0.03% GO by weight cement increased the tensile strength of the mortar by 78.6%, the flexural strength by 60.7% and the compressive strength by 38.9% compared to those of normal cement composites [10]. Babak and his colleagues (2015), studied the mechanical

strength of graphene-cement nano-composites containing 0.1–2 wt% GO and 0.5 wt% super plasticizer and compared with that of cement prepared without GO. They found that the tensile strength of the cement mortar increased with GO content, reaching 1.5%, a 48% increase in tensile strength [14]. M. Murugan and his colleagues (2016), studied the effect of 2D reduced graphene oxide (r GO) sheets on the properties of Portland cement paste in comparison to popularly reviewed nano-materials like aluminum oxide nano- powder ($n\text{-Al}_2\text{O}_3$) and colloidal silicon dioxide nano-particles ($n\text{-SiO}_2$). They found that the addition of 0.02% r GO sheets by weight of cement increased the 7 and 28 days flexural strength up to 70% and 23% respectively when compared to control paste. Moreover, its incorporation substantially decreased the sizes of pores/voids in the paste, even compared to the other nano-materials [15]. Baig Abdullah Al Muhit and his colleagues (2015), investigated about the mechanical properties of cement paste incorporating graphene oxide (GO) with 0.01% and 0.05% dosages and compared with pristine cement paste. Compressive strength tests for Graphene Oxide Cement Composite (GOCC) were carried out on 3, 7, 14, and 28 days. It was observed that GOCC0.05% showed highest compressive strength in all curing ages. It has been assumed that heterogeneous nucleation of C-S-H was responsible for the higher strength gain of GOCC0.05% samples [16].

Several metal oxides of nano-metric dimensions have been created, but the most common ones, because they are produced on a large scale, are probably silica, titanium dioxide and zinc oxide [17]. S.I. Zaki,(2015), studied the effect of adding fly ash (FA) and nano-silica (NS) on the durability of cement pastes under normal and aggressive curing condition .NS was added with different percentages, while FA value was constant (10%) . The samples of the first group were subjected to normal curing and tested after 3 , 7 , 28 days and after one year , while the samples of the second group were subjected to sulphuric acid of concentration 0.2 N and tested after the same ages The study concluded that, there were improvement in the properties of cement pastes when adding NS, as it fills the voids and consume a part of calcium hydroxide leading to additional formation of calcium silicate hydrate (C-S-H) and more improvement of microstructure in both normal and aggressive curing conditions. Adding NS with newly developed super plasticizer (poly-carboxylic ether polymer) improved the durability and strength. Resistance of cementing materials exposed to sulphuric-acid attack can be improved by adding 1% NS and 10% FA (the optimum mix), while adding NS 2% or more and 10% FA leads to more agglomeration in both normal and aggressive curing conditions[18].

M.S. Morsy, and his colleagues (2011), studied hybrid effect of carbon nano-tube and nano-clay on physico-mechanical properties of cement mortar; they used multi wall carbon nano-tubes (MWCNTs) and nano-clays. The nano-clay used in this investigation was nano-kaolin. Nano meta-kaolin (NMK) was added with percentage 6% wt. and the carbon nano-tube was added by ratios of 0.005, 0.02, 0.05 and 0.1 wt. % of cement. The results revealed that adding 6% NMK in cement mortar increases compressive strength by 18%, due to its small particle size, NMK enhances CNTs dispersion. The addition of CNTs (up to 0.02%) to NMK cement mortar improves the compressive strength of the composites with 11% higher than mix containing 6% NMK, while the addition of CNTs by 0.1% decreased the compressive strength [19].

S.I. Zaki and his colleagues (2012), studied the use of activated nano-clay to develop the compressive strength and microstructure of high performance concrete. Nano-clay was added with percentage 0, 3, 5, 7 and 10% by weight of cement. They concluded that the properties of concrete improved by the use of nano-clay since it fills

the voids and consume a part of Calcium Hydroxide leading to more formation of C-S-H and more improvement of interface structure. The application of nano-clay particles with newly developed super plasticizers improved the workability and strength of high performance concrete since nano-clay interpenetrates polymer network and causes the mentioned improvements. The improvement percentages were 36-39-7.6 %, at the ages 3- 7- 28 days respectively [20].

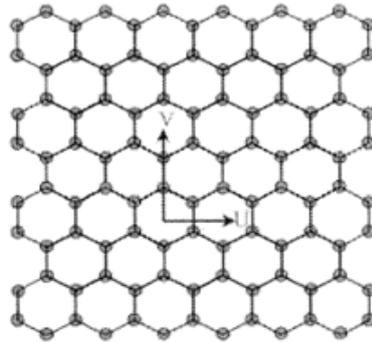


Figure 1: Graphene sheet.

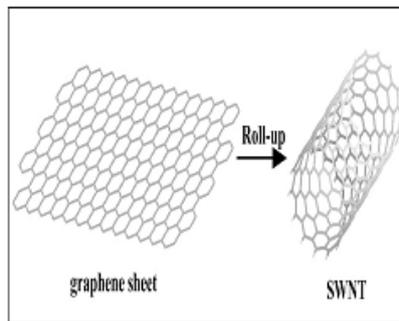


Figure 2 a: Illustration of SWCNTs

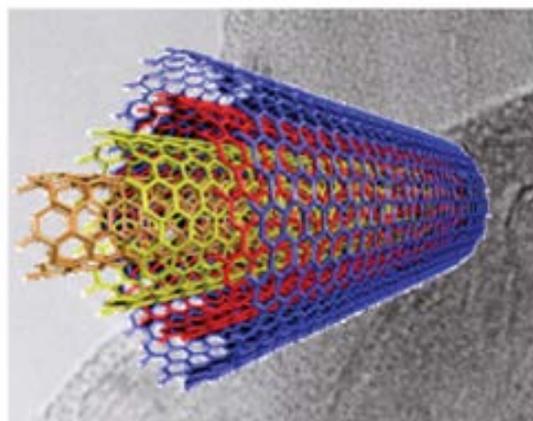


Figure 2 b: Illustration of MWCNTs.

2. Experimental work

In this research, cement mortar without nano-particles was compared with that after the addition of nano-particles. The used materials in the current research were chosen from the available materials in Egypt.

2.1. Materials

2.1.1. Cement

Portland cement produced by Arabian Company was used in all mixes. The grade used was CEM II 42.5N. Testing of cement was carried out according to (ESS: 373/1991 revised to ESS: 242/7 2005). Table 1 shows the physical and mechanical properties of used cement. Table 2 shows the chemical properties of used cement.

Table 1: Physical and mechanical properties of Portland cement used CEM II 42.5N.

Properties	Test result	Limits
Specific weight	3.15	---
Initial setting-time(min)	130	Not less than 60 min
Final setting- time (min)	267	---
Compressive strength of standard mortar	2 days (MPa)=15.3	
	28 days (MPa)=28.6	

The limits are according to Egyptian Standard Specifications (ESS: 373/1991 revised to ESS: 242/7 2005).

Table 2: Chemical composition of Portland cement used CEM II 42.5N.

cement	Chemical analysis (%)
SiO ₂	21.94
Al ₂ O ₃	4.09
Fe ₂ O ₃	3.07
CaO	61.91
MgO	1.81
SO ₃	3.01
L.O.I	3.84
Na ₂ O	0.13
K ₂ O	0.17

2.1.2. Aggregates

Standard aggregate according to (ESS: 373/1991 revised to ESS: 242/7 2005) was used in this research study. Table 3 shows the physical properties of the sand used.

Table 3: Physical properties of sand.

Test	Siliceous sand
Specific weight	2.66
Bulk density (t/m ³)	1.86
Fineness modulus	2.65

2.1.3. Water

Tap water for both mixing and curing was used in this research work.

2.1.4. Nano-materials

2.1.4.1. Graphene sheets

Graphene sheets in this research were brought from Nano Tech Egypt for Photo-Electronics (Communication Center in front of the International School of Choueifat, El-Wahaat Road, Dream land City, Entrance3, City of 6 October, Al Giza, Egypt). Its brand was NT-G-NP. High resolution transmission electron microscopy was performed on JEOL JEM-2100 at an accelerating voltage of 200 KV. Table 4 shows the properties of graphene. Figure 3 shows high resolution transmission electron microscope (TEM) of graphene.

Table 4: Properties of Graphene

Trade name	Graphene sheet
classification	Carbon nano-materials
Chemical type	99 %carbon & 1% oxygen
Appearance (color)	Black
Appearance (form)	Sheet
Density at 50° c (g/ml)	0.88-0.90
Sol. In water	Insoluble
Sol. In solvent	Dispersed in chloroform, hexane
Avg. size (TEM)	100 nm
Shape (TEM)	sheets

2.1.4.2. Nano-silica

Nano-silica (NS) is produced locally and obtained from Nanotechnology laboratory in Housing and Building National Research Center (HBRC), Egypt. Table 5 shows the physical and chemical properties of nano-silica

used. Figure 4 shows high resolution Transmission Electron Microscope (TEM) of nano-silica.

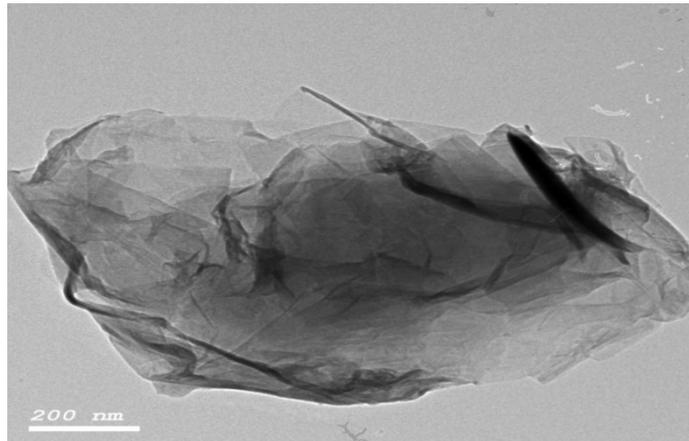


Figure 3: TEM of graphene sheet.

Table 5: Physical and chemical properties of nano-silica

Description	Results
Molecular	SiO ₂
Appearance form	Powder
Color	White
Particle size (nm)	20
Purity (%)	>99.9
Density(25°C)	2.2-2.6g/ml.
Surface area(m ² /g)	400

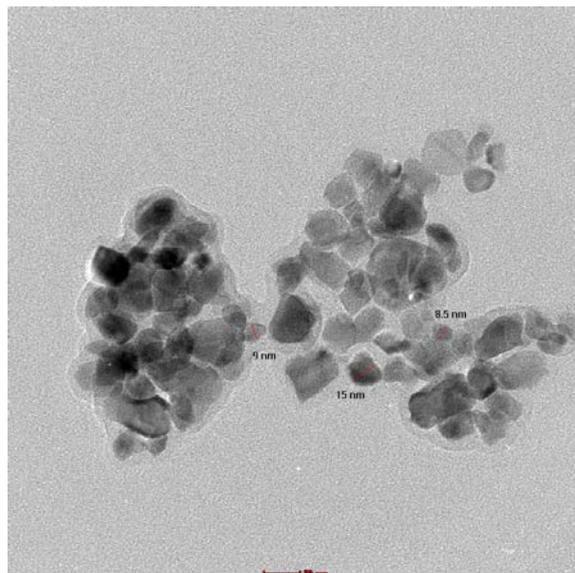


Figure 4: TEM of nano-silica (NS).

2.1.4.3. Nano-clay

Nano-clay (NC) is kaolin clay is produced locally and obtained from Nanotechnology laboratory in Housing and Building National Research Center (HBRC), Egypt. Table 6 shows the physical and chemical properties of nano-clay. Figure 5 shows high resolution Transmission Electron Microscope (TEM) of nano-clay.

Table 6: Physical and chemical properties of nano-clay

Description	Results
Description	Kaolin nano-clay
Appearance form	Powder
Color	Light creamy
Particle size (nm)	100
Purity (%)	>99.9
Surface area(m ² /g)	290

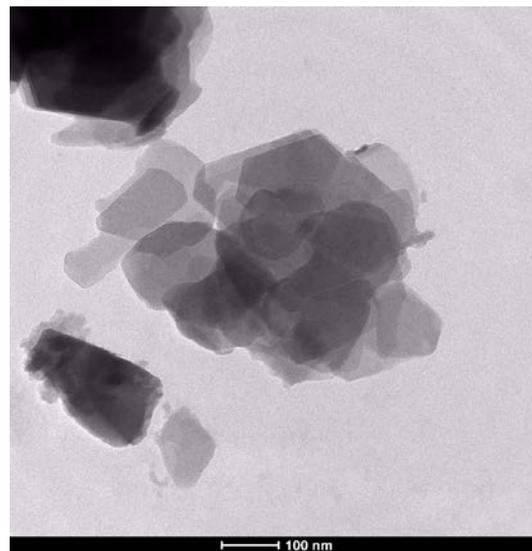


Figure 5: TEM of nano-clay (NC).

2.2. Mix design

Four mix groups were designed in this study. Cement and standard sand is homogenized and mixed with water with ratio (1:3:0.4) respectively according to Egyptian specifications (ESS: 373/1991 revised to ESS: 242/7 2005). Table 7 shows the composition of cement mortar with and without nano-particles.

2.3. Mixing procedure and sonication technique

To get cement mortar with and without nano-particles, the following steps were conducted:

- 1) The first group which is the control group of all groups (GP1); cement and standard sand is homogenized then mixed with tap water where no nano-particles were added to the mixture.
- 2) The second group (GP2); graphene nano-sheets were used with ratios (0.04%; 0.05%; and 0.06 wt. %) of cement material. The three different ratios were weighted by using the sensitive balance apparatus (its accuracy is 0.00001 gm), Figure 6 shows the sensitive balance apparatus. The cement and standard sand were mixed for 1.0 minute, then (75%) of mixing water was added, each ratio of graphene (0.04%;0.05%;0.06%)by weight of cement was pre-solved in (1%) of chloroform using sonica motor for 1 min. ,Table 8 shows the physical and chemical properties of chloroform, Figure 7 shows the sonica motor, then (25%) of the remaining mixing water was added to this mixture and remixed again using sonica motor for another 3 minutes, then the mixture was added to the cement mortar and mixed for 2 minutes in mortar mixer, Figure 8 shows the mortar mixer.
- 3) The third group (GP3); hybrid nano-particles (graphene nano-sheets with ratios; 0.03%; 0.04%; and 0.05% by wt. and optimum ratio of nano-silica (1%) according to ref. [21]) were added to cement mortar. The same mixing and dispersion techniques were used.
- 4) The fourth group (GP4); hybrid nano-particle (graphene nano-sheets with ratios; 0.03%; 0.04%; and 0.05% by wt. and optimum nano-clay (5%) according to ref. [21]) were added to cement mortar. The same mixing and dispersion techniques were used.



Figure 6: The sensitive balance device.



Figure 7: Sonica Motor.



Figure 8: Mortar Mixer.

Table 7: Mix proportions of cement mortar with and without nano-materials.

Group	Group Description	Mix Proportions for 1M3 of cement mortar					
		Cement CEMII42.5N (kg/m ³)	Siliceous Sand (kg/m ³)	Water (cm ³ /m ³)	Nano-materials		
					Graphene sheets (gm)	Nano- Silica (kg)	Nano- Clay (kg)
GP1	Control group	555	1665	222	-----	-----	-----
GP2	0.04% graphene	554.78	1665	222	0.222	-----	-----
	0.05% graphene	554.72	1665	222	0.2775	-----	-----
	0.06% graphene	554.66	1665	222	0.333	-----	-----
GP3	(0.03% graphene + 1% nano-silica)	549.28	1665	222	0.1665	5.55	-----
	(0.04% graphene + 1% nano-silica)	549.22	1665	222	0.222	5.55	-----
	(0.05% graphene + 1% nano-silica)	549.17	1665	222	0.2775	5.55	-----
GP4	(0.03% graphene + 5% nano-clay)	527	1665	222	0.1665	-----	27.75
	(0.04% graphene + 5% nano-clay)	527	1665	222	0.222	-----	27.75
	(0.05% graphene +5% nano-clay)	526.97	1665	222	0.2775	-----	27.75

Table 8: Physical and chemical properties of chloroform.

Description	Results
Molecular formula	CHCl ₃
Appearance form	Dense liquid
Color	colorless
Density(25°C)	1.489g/cm ³
odor	Sweet-smelling
Molar mass	119.37g/mol
Thermal conductivity(20°C)	0.13W/m.K

2.4. Specimen preparation

The mixtures were casted in steel mold cubes used for mortar of dimensions (70x70x70) mm for compressive strength test, and a steel mold prism of dimensions (40x40x160) mm was used for flexural strength test. After pouring the mixes into molds, an electric vibrator was used to ensure good compaction.

All specimens were remolded 1 day after casting. Thereafter, they were cured in standard water tank at 21±2°C until testing at age 2, 7 and 28 days.

2.5. Thermal conductivity

KD2 thermal conductivity device was used to determine thermal conductivity (K-value) for the optimum specimen cube of dimension (70x70x70) mm at age 28 days from different mortar mixes of the four groups. Figure 9 shows the KD2 thermal conductivity device.

The test took place in physics department laboratory of the Housing and Building National Research Centre (HBRC), Egypt. The test was conducted to the standard specification ASTM D5334. The environmental test conditions: [temp. =24 oC &R.H. =55%].

2.6. Scanning electron microscopy

Scanning electron microscopy (SEM) test was carried out in physics department laboratory of the Housing and Building National Research Centre (HBRC), Egypt to characterize the topography of the optimum specimen cube of dimension (70x70x70) mm from different mortar mixtures of the four groups which interpret the compressive strength results at age 28 days.

The test was made using Inspect-S microscope. Figure 10 shows SEM apparatus. The test requirements were performed according to ISO/IEC17025. The environmental test condition is [temp. =23 oC &R.H. =57%].



Figure 9: Thermal conductivity device



Figure 10: Scanning Electron Microscope (SEM).

3. Result and discussion

3.1. Compressive strength of mix proportions for different cement mortar mixes

Table 9 demonstrates the compressive strength for all cement mortar mixes at ages of 2, 7 and 28 days.

Table 9: Compressive strength results of cement mortar with and without nano-materials.

Mix No.	Group description	Compressive strength (MPa)			Notes
		2days	7days	28days	
M0	Cement mortar only(control)	15.27	21.93	28.5	Control group (GP1)
M1	0.04% graphene+control	17.73	27.2	36.67	Graphene group (GP2)
M2	0.05% graphene+control	21.33	30.07	38.8	
M3	0.06% graphene+control	20.53	24.4	28.27	
M4	0.03% graphene+1%NS+control	17.47	23.27	29.07	(Graphene+1%NS)group (GP3)
M5	0.04% graphene+1%NS+control	16.4	21.1	25.8	
M6	0.05% graphene+1%NS+control	13.07	18.67	24.4	
M7	0.03% graphene+5%NC+control	11.87	13.17	14.47	(Graphene+5%NC)group (GP4)
M8	0.04% graphene+5%NC+control	10.2	11.67	12.5	
M9	0.05% graphene+5%NC+control	2.2	3.9	5.6	

3.1.1. Graphene sheets

Figure 11 shows the compressive strength results of mix proportions of graphene sheets ratios which were added to cement mortar at age 2, 7 and 28 days. It can be seen that compressive strength of adding 0.05 by wt. % of graphene sheets to mortar was improved at age 28 days to reach 35.66% with respect to the control mix which considered being the optimum ratio of graphene sheets.

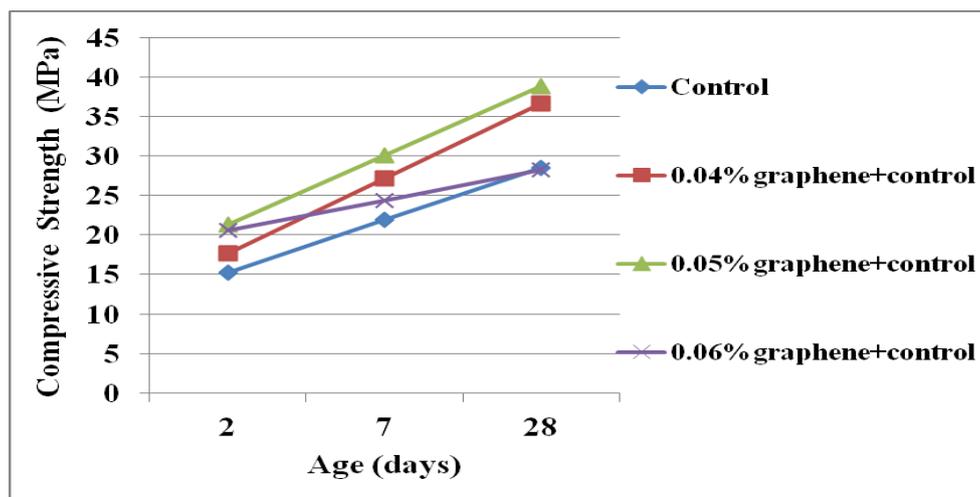


Figure 11: Effect of graphene sheet of different mixes with cement mortar on compressive strength.

3.1.2. Hybrid nano-materials

3.1.2.1. Graphene sheets with nano-silica

Figure 12a shows the compressive strength results of different mix proportions of graphene sheets ratios and 1% nano-silica (NS) to cement mortar at age 2, 7 and 28 days. It can be seen 2.00% improvement in compressive strength result was obtained by optimum hybrid nano-materials mix of ratio (0.03% graphene sheets and 1% nano-silica) by weight of cement content at age 28 days with respect to the control mix which conclude that no significant increase in the compressive strength of cement mortar with (graphene ratios and 1% nano-silica) at age 28 days with respect to the control mix.

3.1.2.2. Graphene sheets with nano-clay

Figure 12b shows the compressive strength results of different mix proportions of graphene sheets ratios and 5% nano-clay (NC) to cement mortar at age 2, 7 and 28 days.

It can be seen a decrease in the compressive strength results of cement mortar with (graphene ratios and 5% nano-clay) at age 28 days with respect to the control mix. It can be explained because of the agglomeration caused by the nano-clay particles when adding excessive amount as the high surface area increases, these particles were attracted to each other forming weak clogs.

These clogs fill the voids of the mortar mixture preventing the filling effect of nano-particles decreasing the mixture strength.

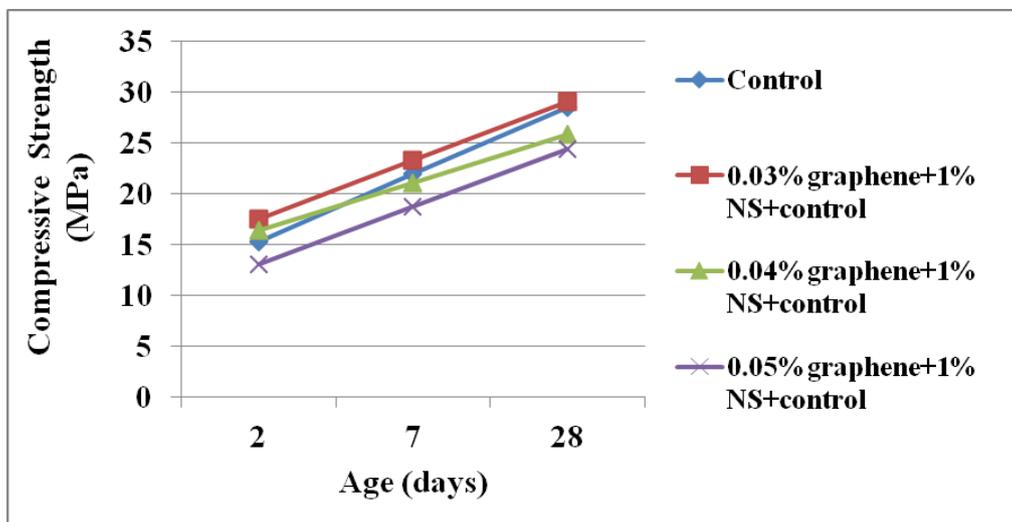


Figure 12 a: Effect of graphene and 1% NS of different mixes with cement mortar on compressive strength

3.2. Flexural strength of mix proportions for different cement mortar mixes

Table 10 demonstrates the compressive strength for all cement mortar mixes at ages of 2, 7 and 28 days.

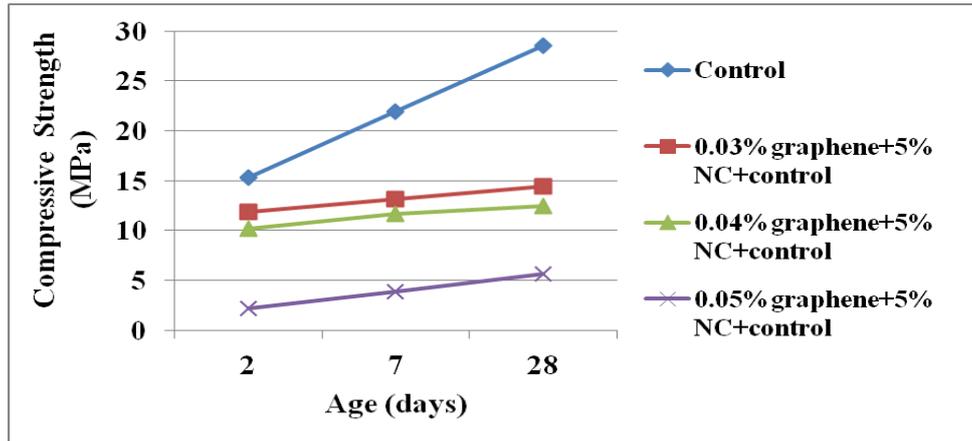


Figure 12 b: Effect of graphene and 5% NC of different mixes with cement mortar on compressive strength.

Table 10: Flexural strength results of cement mortar with and without nano-materials.

Mix No.	Group description	Flexural strength (MPa)			Notes
		2days	7days	28days	
M0	Cement mortar only(control)	7.03	7.54	8.04	Control group (GP1)
M1	0.04% graphene+control	7.30	8.35	9.40	Graphene group (GP2)
M2	0.05% graphene+control	8.04	9.38	10.72	
M3	0.06% graphene+control	7.69	8.06	8.42	(Graphene+1 %NS) group (GP3)
M4	0.03% graphene+1% NS+control	7.18	7.78	8.37	
M5	0.04% graphene+1% NS+control	6.88	6.95	7.013	
M6	0.05% graphene+1% NS+control	6.48	6.64	6.79	(Graphene+5% NC) group (GP4)
M7	0.03% graphene+5% NC+control	7.03	7.103	7.18	
M8	0.04% graphene+5% NC+control	6.90	7.00	7.10	
M9	0.05% graphene+5% NC+control	5.16	5.77	6.36	

3.2.1. Graphene sheets

Figure 13 shows the flexural strength results of different mix proportions of graphene sheets ratios added to cement mortar at age 2, 7 and 28. It can be seen that adding 0.05 by wt. % graphene sheets to cement mortar improved the flexural strength by 33.33% with respect to the control mix at age 28 days which considered being the optimum ratio of graphene sheets.

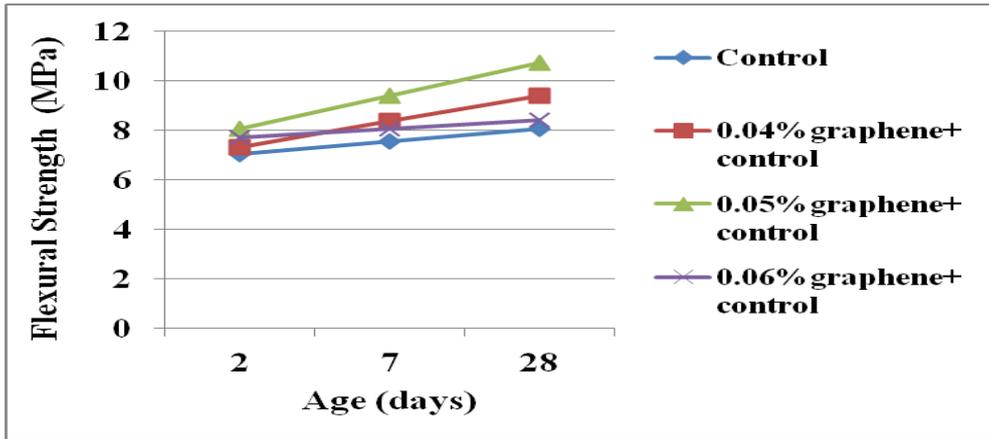


Figure 13: Effect of graphene of different mixes with cement mortar on flexural strength.

3.2.2. Hybrid nano-materials

3.2.2.1. Graphene sheets with nano-silica

Figure 14a shows the flexural strength results of cement mortar mixes at age 2, 7 and 28 days with addition of graphene sheets of different ratios and 1% nano-silica (NS) to cement mortar. It can be seen that the improvement in flexural strength result reached 4.10% for optimum mortar mix of hybrid nano-materials of ratio (0.03% graphene sheets and 1% nano-silica) by weight of cement content at age 28 days with respect to the control mix which considered being no significant increase in the flexural strength of cement mortar with (graphene ratios and 1% nano-silica) at age 28 days with respect to the control mix.

3.2.2.2. Graphene sheets with nano-clay

Figure 14b shows the flexural strength of cement mortar mixes at age 2, 7 and 28 days with addition of graphene sheets of different ratios and 5% nano-clay (NC) to cement mortar. It can be seen that a decrease in the flexural strength results of cement mortar with (graphene ratios and 5% nano-clay) at age 28 days with respect to the control mix.

It can be explained because of the agglomeration caused by the nano-clay particles when adding excessive amount as the high surface area increases, these particles were attracted to each other forming weak clogs. These clogs fill the voids of the mortar mixture preventing the filling effect of nano-particles decreasing the mixture strength.

3.3. A comparison of the results of compressive strength for cement mortar with and without nano-materials

The comparison between the results of the compressive strength of the optimum mix proportions for different cement mortar mixes from the four groups at the age of 28 days is shown in figure 15.

It is shown that the optimum sample of cement mortar with graphene sheet 0.05 by wt. %) gave better

results(35.66%) than optimum samples of cement mortar contains hybrid nano-materials used in this research with respect to the control ones .

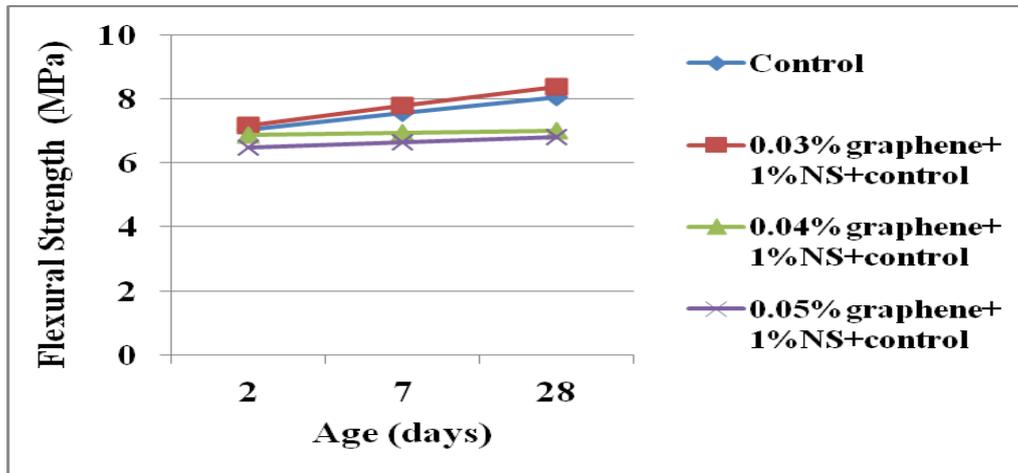


Figure 14 a: Effect of graphene and 1% NS with cement mortar of different mixes on flexural strength

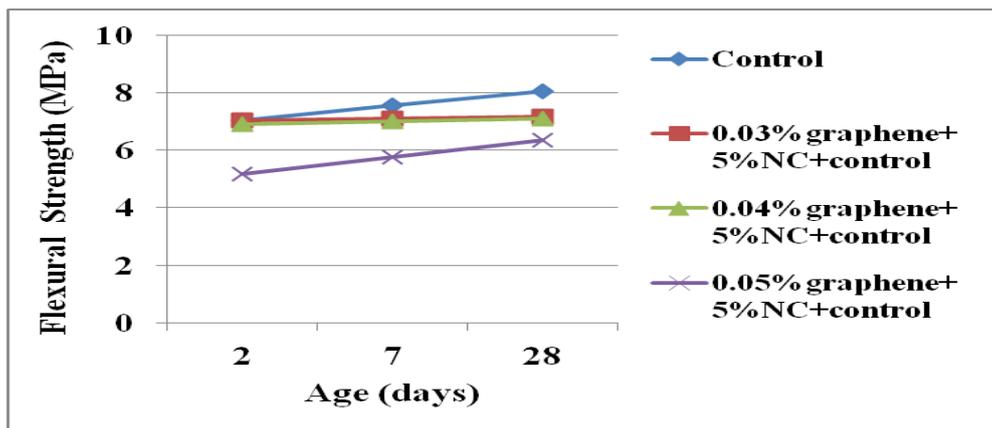


Figure 14 b: Effect of graphene and 5%NC with cement mortar for different mixes on flexural strength.

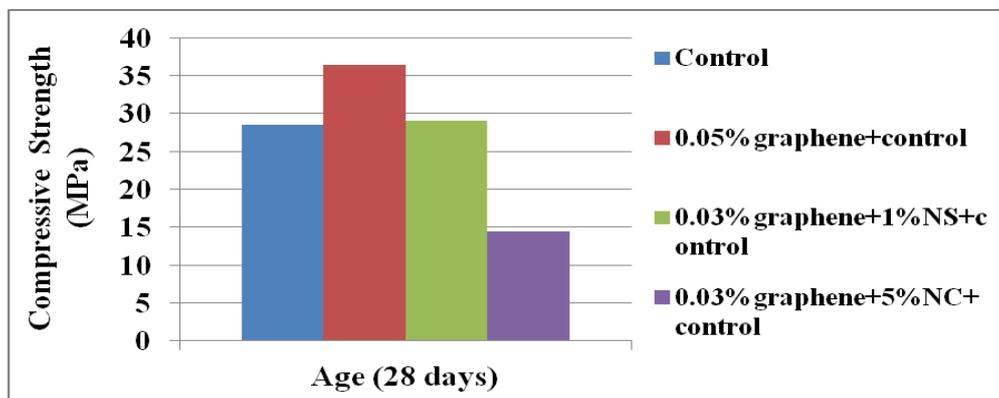


Figure 15: Relationship between compressive strength results of control and added optimum nano-materials to control at age 28 days.

3.4. A comparison of the results of flexural strength for cement mortar with and without nano-materials

The comparison between the results of the flexural strength test of the optimum mix proportions for different cement mortar mixes from the four groups at the age of 28 days is shown in figure 16. The optimum sample of cement mortar with 0.05 by wt. % graphene sheet gave better results (33.33%) than optimum samples of cement mortar contains hybrid nano-materials used in this research with respect to the control ones.

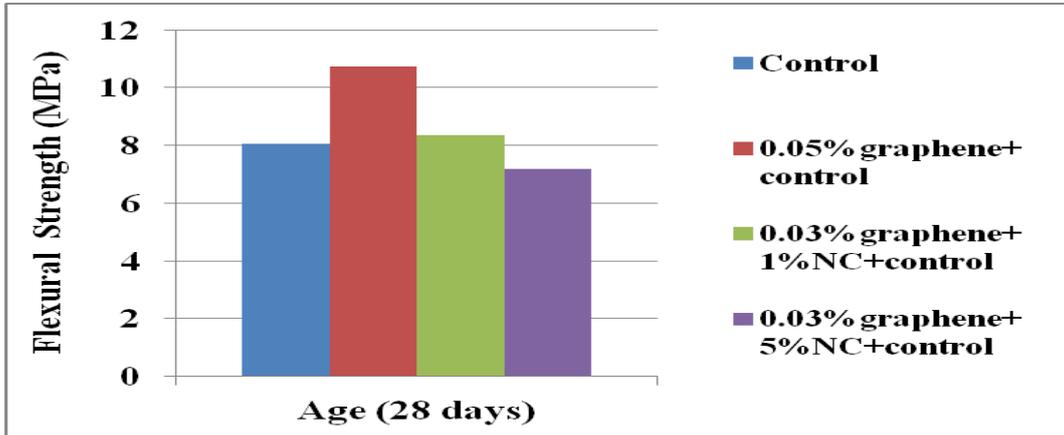


Figure 16: Relationship between flexural strength results of control and added optimum nano-materials to control at age 28 days.

3.5. Thermal conductivity results

Figure 17 indicates the thermal conductivity results of the optimum mix proportions for different cement mortar mixes from the four groups at the age of 28 days. it is shown that the optimum ratio of 0.05 by wt.% graphene sheet with cement mortar gave low thermal conductivity result with a rate of 6.36% than the optimum samples of cement mortar contains hybrid nano-materials used in this research with respect to the control ones .

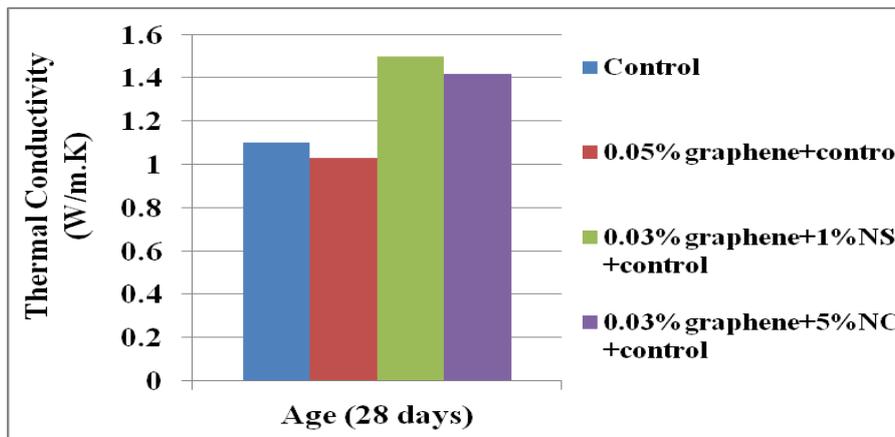


Figure 17: Thermal conductivity results of control and added optimum nano-materials to control at age 28 days.

3.6. Sem results

Figure 18a; 18b; 18c; and 18d demonstrate the SEM micrograph of the optimum cement mortar mixes of four groups at age of 28 days to analyze their topography, morphology, composition, and crystallographic information. SEM micrographs in figure 18b of the optimum sample of cement mortar contain 0.05 by wt. % graphene sheet shows more refined microstructure, very smaller pores and more compaction formation of hydration products compared to control mix were achieved, which can lead to an enhanced improve in physico-mechanical properties of cement mortar. While SEM microstructure in figure 18c and 18d of optimum samples of cement mortar contains hybrid nano-materials used in this research show more voids, unrefined microstructure due to the reduction content of $\text{Ca}(\text{OH})_2$ crystals with respect to control mix which can lead to decrease in physico-mechanical properties of cement mortar as they cannot act as filler and an activator which promotes the hydration process.

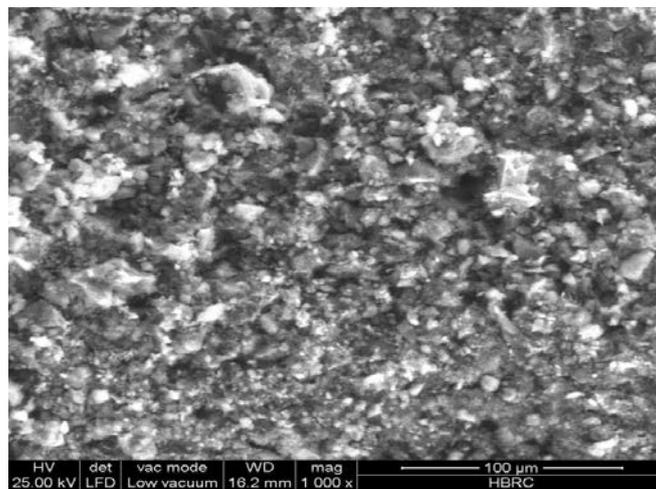


Figure 18a: SEM control sample at age 28 days.

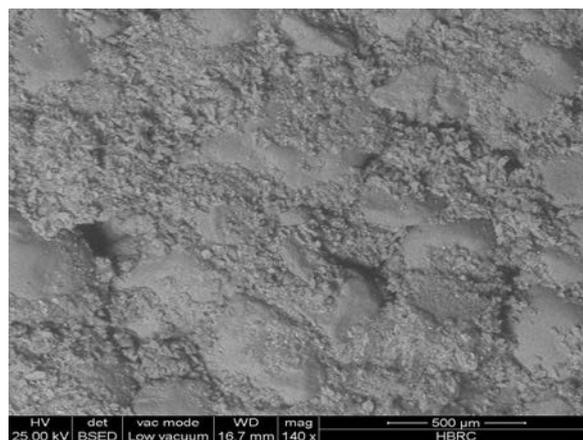


Figure 18 b: SEM of (0.05% graphene+ control) sample at age 28 days.

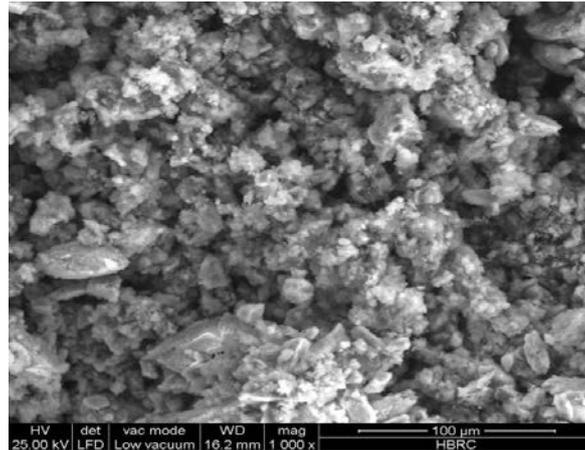


Figure 18 c: SEM of (0.03%+1%NS+control) sample at age 28 days.

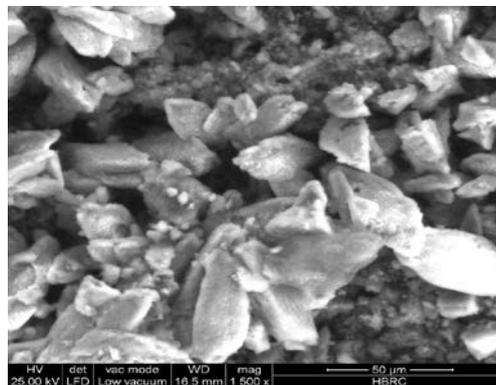


Figure 18d: SEM of (0.03%+5%NC+control) sample at age 28 days.

3.7. Statistical results

Statistical analysis results were carried out using “Statistical Package for Social Sciences” (SPSS) program for different mortar mixes groups without and with nano-particles with different percentages at the ages of 2,7 and 28 days. It is concluded that the performance of using 0.05 by wt. % graphene sheets only with cement mortar without adding any other nano-materials was better in comparison than added to other two nano-materials, despite the significantly lower amounts that were used in mortar.

4. Conclusion

Based on the study reported here, the following conclusions are drawn:

- The optimum ratio of graphene is 0.05% by weight and the optimum dose of graphene in hybrid nano-materials is 0.03%.
- The improving percentage of compressive strength of cement mortar when graphene was added reached 35.66% with respect to the control mixes.
- The improving percentage of flexural strength of cement mortar when graphene was added reached

33.33% with respect to the control mixes.

- Low thermal conductivity was achieved to reach 6.36% when adding ratio of 0.05% graphene by weight compared to control ones.
- According to the SEM micrographs, more refined microstructure and very smaller pores were achieved by addition of 0.05% graphene by weight compared to control ones, which can lead to an enhanced improve in physico-mechanical properties of cement mortar.
- The SEM micrographs of hybrid nano-particles (graphene + 1% nano-silica) or (graphene + 5% nano-clay) show more voids and unrefined microstructure which can lead to decrease in physico-mechanical properties of cement mortar as they cannot act as filler and an activator which promotes the hydration process.
- Statistical analysis results showed high significant when adding 0.05% graphene by weight without adding any other nano-materials than hybrid nano-materials used in this research, despite the significantly lower amounts that were used in mortar.

Acknowledgement

Authors wish acknowledgement to appreciate staff of Structural Engineering Department of Faculty of Engineering, Mansoura University for their cooperation and encouragement.

References

- [1] B.A. Al Muhit, L. Boo Hyun Nam, J. Zhai, Zuyus. (2015), "Effects of Microstructure on the Compressive Strength of Graphene Oxide-Cement Composites." *Nanotechnology in Construction*, 1-9
- [2] M. Gamil, K. Nakamura, A. Fath El-Bab, O. Tabata, M. Serry, A. Abd El-Moneim."Investigation of Graphene Piesoresistivity based on density functional theory." Fifth International Conference on Nano-Technology in Construction (NTC2013), Cairo, Egypt 2013; 23-25 March
- [3] Internet: www.en.wikipedia.org/wiki/Graphene, visited on August-15-2011.
- [4] C. Ostiguy, B. Roberge , C. Woods, B. Soucy.(2010), "Engineered Nano-particles: Current Knowledge about Occupational Health and Safety Risks and Prevention Measures IRSST." Second Edition
- [5] F. Sanchez, K. Sobolev. (2010), "Nanotechnology in concrete – A review." *Construction and building materials*, 24, 2060
- [6] K. Sobolev, I. Flores, R. Hermosillo, M. Leticia, T. Martinez.(2006; November 7)," Nano-materials and nanotechnology for high –performance cement composites", Denver, USA
- [7] Internet: The 2010 Nobel Prize in Physics- Press Release, NobelPrize.org. 1 Nov.2011.
- [8] Z. Fan.(2014), "Investigation on properties of cementitious materials Reinforced by Graphene." University of Pittsburgh
- [9] I.D. Rosca, F. Watari, M.Uo, T.Akasaka. (2005)," Oxidation of multi-walled carbon nano-tubes by nitric acid, *Carbon*." 43(15), 3124
- [10] SH. Lv, YJ. Ma, CC. Qiu, T. Sun, JJ. Liu, QF.Zhou. (2013), "Effect of graphene oxide nano sheets of micro structure and mechanical properties of cement composites." *Constr Build Master*, 49,121
- [11] A. Sedaghat, et al. (2014), "Investigation of physical properties of graphene-cement composite for

structural applications.” Article ID: 41685, 4 (1), 12

- [12] Z. Pan, L. He, L. Qiu, A.H. Korayem, , Li G., J.W. Zhu, F. Collins, D. Li, W.H. Duan, M.C. Wang.(2015), “Mechanical properties and microstructure of a graphene oxide-cement composite.” *Cement and Concrete Composites*
- [13] K. Gong, Z. Pan, A. Korayem, , L. Qiu, D. Li, F. Collins, W. Duan. (2014), “Reinforcing Effects of Graphene Oxide on Portland cement Paste.” *J. Mater. Civ. Eng. Journal of Materials in Civil Engineering*
- [14] F. Babak, H. Abolfazl, R. Alimorad, G. Parviz. (2015; July 10), “Preparation and Mechanical Properties of Graphene-Oxide: Cement Nano-composites.” *The Scientific World Journal*, 2014, 1-10.
- [15] M. Murugan, M. Santhanam, S.S. Gupta, T. Pradeep, P. Surendra. (2016), “Influence of 2D r GO nano-sheets on the properties of OPC paste.” *Cement and Concrete Composites*, 70, 48
- [16] B. Abdullah Al Muhit, B. Boo Hyun B., L. Zhai, J. Zuyus. (2016),” Effect of Microstructure on the Compressive Strength of Graphene Oxide-Cement Composites.”, *Nanotechnology in Construction*
- [17] ICON, (2008; May 1),”Towards Predicting Nano-Bio interactions: An International Assessment of Nanotechnology Environment, Health and Safety Research Needs.” *International Council on Nanotechnology*,4,80
- [18] S.I. Zaki. “Assessment of the Durability of Nano- Silica / Fly Ash Cement Pastes Exposed to Normal and Aggressive Curing Conditions.” *Seventh International Conference On Nanotechnology in Construction (NTC 2015)*, Sharm El-Sheikh, Egypt,2015;March
- [19] M.S. Morsy, S.H. Alsayed, M. Aqel. (2011), “Hybrid Effect of Carbon Nano-tube and Nano-Clay on Physico-Mechanical Properties of Cement Mortar.” *Construction and Building Materials* 25, 145.
- [20] S.I. Zaki and I. Sobhy. (2012; July 9-11),”The Use of Activated Nano-Clay to Develop the Compressive Strength and Microstructure of High Performance Concrete”, *CTU Conference, Concrete in the Low Carbon Era*, the University of Dundee, UK
- [21] M.A.M. Sonosi. (2015), “The effect of using nano-materials on the properties of cement paste and mortar.” *MSc, Faculty of engineering, Cairo University, Giza, Egypt*