Utilization of Nano Clay, Marble Powder and Silica Fume Waste as Hybrid Addition for Enhancing the Properties of Concrete

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***Abstract*- The main objective of this research is to investigate the effect of utilizing Nano Clay (NC) particles and Marble Powder (MP) in Normal Strength Concrete (NSC) and in High Strength Concrete (HSC) on its physical/mechanical properties and microstructure configuration. For obtaining economically feasible concrete mix, the amount of NC particles in the mix was reduced by MP as a cheap waste material. This reduction of NC particles also facilitated its dispersion in partial amount of mixing water and superplasticizer by practical techniques such as, stirring and sprinkling. At first, concrete samples were prepared with hybrid additions of NC and MP; NC and MP replacement ratios were 3% and 5% of cement and 5%, 10% and 15% of sand by weight, respectively. After that, concrete physical properties; permeability, and mechanical properties; compressive, flexural, splitting and bond strength were investigated. Moreover, stress-strain response of optimum performance mixes was monitored. Finally, the microstructure of these mixes was studied using Scanning Electron Microscopy analysis (SEM) and Thermogravimetric Analysis (TGA). It can be concluded from this work that the best physical/mechanical performance of concrete mixes can be achieved by using 3% NC and 10% MP additives ratios by weight of cement and sand, respectively. Also, the microstructure of these mixes shows less voids due to filling effects of MP and the share of NC in the hydration process.**

Keywords*- *Nano clay, marble powder, silica fume, hybrid additions, waste, sprinkling, dispersion.

1. INTRODUCTION

Developing and enhancing the properties of green concrete has lately drawn the attention of researchers due to the widespread use of concrete in construction field. Many researches had studied methods of producing environmentally friendly concrete to be convenient as green construction material [1–6]. There are significant improvements in mechanical and physical properties of concrete when partially substitute its cementing material by pozzolanic materials as fly ash, slag, silica fume, and metakaolin, furthermore, the friendly effect on the environment is significant [7–10]. Also, non-pozzolanic materials, which are industrial byproducts or waste materials, like marble, granite and limestone powders can be used as partial substitute to cement or aggregates. This can improve concrete properties by packing the cement matrix structure. Moreover, neglecting handling waste materials causes environmental problems and negative impacts on the sustainable development; hence, the reuse of waste materials to reduce hazards to the environment is adopted by most countries [11–13].

Egypt is recognized as one of the top five in the world in marble industry. For instance, industrial zone known by Shaq Al-Thuban located in the Capital of Egypt has lots of marble factories that produce around 500,000 tons of waste per year [14]. This situation represents a significant problem to the environment in Egypt, but in the same time it can be considered as a motivation for the scientific community to adopt reusing this waste in the green concrete production industry.

Nowadays, nanotechnology plays a key role in the development of more durable green concrete as the matter of fact that the performance of concrete composites like mechanical properties and durability begins from its nanostructure. Nanotechnology can be defined as restructuring materials (at least one of its dimensions) to a scale less than 150 nm for acquiring new properties and functions [15]. The two classifications of nanomaterials are pozzolanic (nano silica, titanium, calcium and nano clay), and fiber (carbon nanotubes and carbon nanofiber). Pozzolanic reaction forms additional calcium silicate hydrate (C-S-H) by consuming calcium hydroxide crystals in hydrated cement leading to the improvement of cement matrix [16–23]. While fiber nanomaterials strengthens the cement matrix in tensile strength by acting as bridge connecting both sides of the crack together preventing crack propagation [24–27].

NC, manufactured by metakaolin based material, integrates both features of the two categories of nanomaterials. Its particles are in shape of sheets and are characterized by elongated, thin and flake configuration. These sheets are formed to an extent of silicate mineral that increases pozzolanic activity. In addition, it is characterized by simple manufacturing and local availability in Egypt [18,22,28–31].

The main hurdle in using NC as an additive to concrete mixture is the discrepancies in literature about defining its optimum ratio in concrete mixes. Many authors attributed that to the dispersion techniques of NC during mixing. Defective dispersion forms NC agglomerations in the matrix causing weak clogs that restrict the hydration process [32–34]. Authors previously applied several dispersion techniques as stirring and sonicating to solve agglomeration problem [32–34].

Serag et al [35] reported that introducing the required mixing water by sprinkling technique, which is simple and applicable, was more effective in enhancing concrete properties compared to traditional technique; pouring the required mixing water directly into mixer. Moreover, using sprinkling technique reduced the mixing water content while maintaining the mechanical and physical properties of concrete at their ultimate levels.

Natarajan et al [36] investigated utilizing different amount of MP and green sand as fine aggregate hybrid replacement, besides, constant percentage (5%) of metakaolin as cement replacement, by weight, on the strength and durability of concrete. It was noticed that the additions declined the workability of mixes due to agglomeration of metakaolin. The authors attributed that unfavorable situation to the increased demand for mixing water, resulted from the constant ratio of the superplasticizer used for all mixtures. However, incorporation of these powders in concrete improved strength and durability compared to normal concrete. The optimum percentage was 15% for both replacements of fine aggregate by weight.

Hamed et al [30] found that, Adding de-agglomerated NC particles using sonication and dispersion techniques in concrete mixture was more effective in enhancing mechanical properties compared to adding NC as-received. The optimum ratio of NC as cement substitution was 7.5% by weight for both dispersion techniques. SEM analysis did not detect NC agglomeration in case of sonication and the produced concrete was well compacted, while agglomeration was observed with the other technique.

Alimohammad et al [31] reported that, the addition of NC as cement replacement increased the viscosity of Self-Consolidating Concrete (SCC) which prevented the segregation and bleeding of fresh mixture. NC improved mechanical properties of SCC especially at early ages in addition to increasing its durability. The ratios of NC were 1%, 2% and 3% by weight of cement, and the best improvements in test results were observed at 3%.

Aliabdo et al [14] reported that, reusing MP as sand replacement was more effective in enhancing mechanical properties of concrete compared to using it as cement replacement. In addition, both replacements of marble produced less porous concrete compared to conventional concrete. Using 10% of MP as a partial replacement of either cement or sand by weight revealed the best improvements in that study.

Omar et al [37] found that, the use of limestone waste as sand replacement and marble powder as an additive in concrete has more significant effect on the mechanical and permeability properties of concrete. The enhancements were revealed with MP up to 15%.

Hameed et al [38] recommended that, replacing fine aggregates with 85% of crushed rock dust and 15% of MP improved strength and durability of SCC. In addition, the combined effect of replacements revealed a significant enhancement in the segregation resistance.

2. RESEARCH SIGNIFICANCE

This study focuses on the ability of producing green concrete with NC and MP additives. Introducing these additives in the mix is more favorable to environment as it decreases the use of cement and aggregates in the mix which, in consequence, minimizes CO_2 emissions of cement manufacturing and aggregate quarrying processes.

As can be concluded from the available literature, there is no clear range of the optimum NC ratio to be added to concrete mix. Moreover, numerous researchers studied the effect of adding only NC on the performance of concrete. Therefore, the hybrid use of NC and MP is implemented in this study. This technique of using hybrid additives in producing concrete mix is suggested by the authors to reduce the amount of NC additive in the mix. This reduction would lead to also minimizing mix cost besides its environmental benefits. Also, effect of various NC dispersion techniques on mix mechanical properties is studied to overcome agglomeration problems.

3. EXPERIMENTAL WORK

The experimental work was divided to three parts. In the first part the effect of increasing NC ratio with various dispersion techniques on mortar strength was studied and the optimum NC ratio was determined. In the second part, the effect of MP ratio on the ratio of NC was studied. The optimum ratio of NC and MP that results in the highest concrete compressive strength was determined at this stage. In the third part of this experimental program, compressive strength, flexural strength, splitting strength, bond strength, stress strain behavior and permeability of NSC and HSC concrete modified with the optimum percentages of hybrid additions obtained from part two were studied and compared to NSC and HSC. In addition, TGA and SEM analysis verified the hardened concrete microstructure.

3.1 Materials

Materials used in this study are as follows:

- Ordinary Portland Cement (OPC) (CEM I/52.5R) in accordance with ASTM C150 [39].
- Natural siliceous sand was used as fine aggregates with fineness modulus of 2.5
- Crushed clean dolomite was used as coarse aggregates with nominal maximum size of 19.0 mm.
- Mineral admixtures as NC, MP and Silica Fume (SF) were used as hybrid additions for NSC and HSC.

The NC used in this study, known as nano-metakaolin, is formed from thermal activation (dehydroxylation) of kaolin at 800^{o}C. This activation process led to converting the crystal lattice structure to amorphous substance that has high pozzolanic activity. The mean particle size distribution of NC was 87.13 µm as shown in Fig. 1. Transmission Electron Microscopy (TEM) micrograph of NC shows the particles in shape of sheets that characterized by elongated, thin and flake-shaped particles, as shown in Fig. 2. The mean particle size distribution of MP was 7.25 µm as shown in Fig. 3. TEM micrograph of MP shows spherical shape particles as presented in Fig. 4. XRD analysis presented in Fig. 5 shows calcite composition and crystalline lattice of MP particles. Silica Fume (SF) is a condensed fine powder which has high pozzolanic activity and is a byproduct of the manufacture of silicon or ferro-silicon alloy. Silica fume corresponds with the requirements of ASTM C 1240-15 [40]. High Performance Superplasticizer (SP), which is an aqueous solution of modified polycarboxylates, was used to obtain a required average slump within range of 100 to 200 mm. SP complies with EN 934-2

[41]. Tap water was used for both mixing and curing. Chemical composition of cement, NC and SF are presented in Table 1.

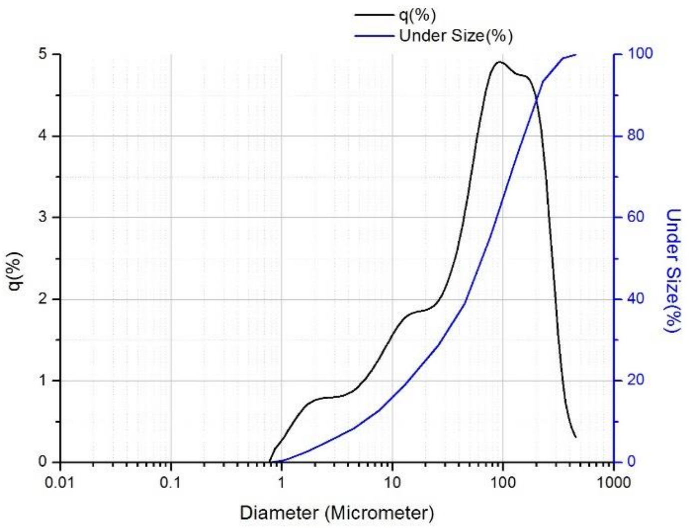

Fig. 1. Particle Size Distribution of NC.

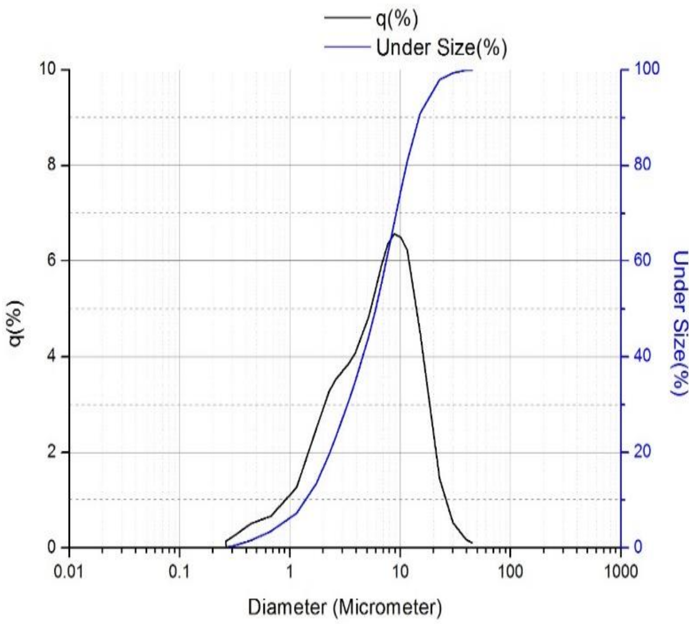

Fig. 3. Particle Size Distribution of MP.

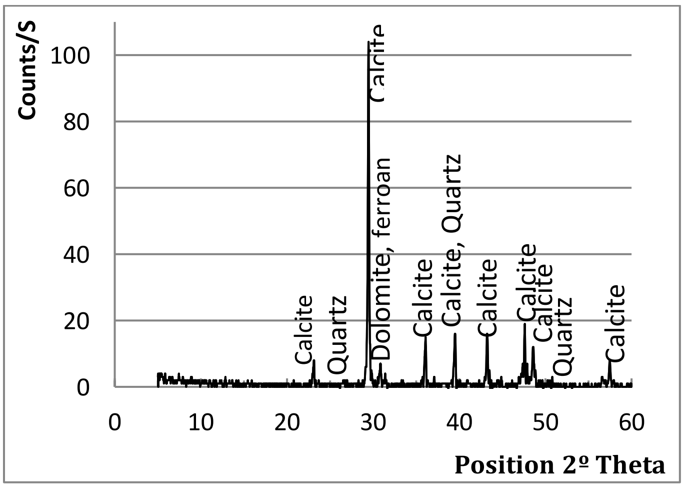

Fig. 5. XRD Analysis for MP.

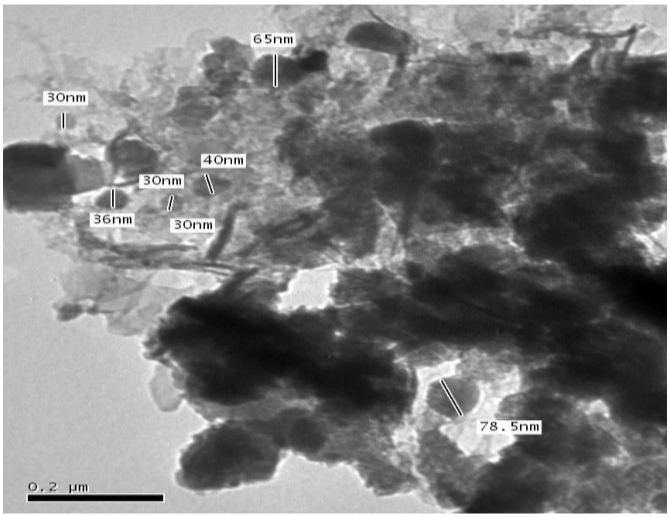

Fig. 2. TEM Micrograph of NC.

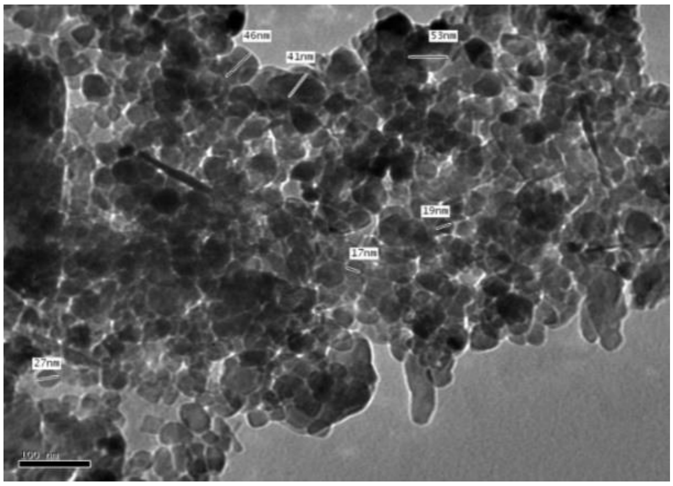

Fig. 4. TEM Micrograph of MP.

Table 1. Chemical Composition of Cement, NC and SF.

%	CEM I 52.5	NC	SF
SiO2	19.8	59.20	90.20
Al2O3	5.5	26.75	1.70
CaO	63	0.10	2.1
MgO	1.2	<0.10	1.70
Fe2O3	3.4	1.17	0.40
Na2O	0.64	<0.10	0.70
K2O	0.19	0.06	0.70
SO3	3	---	0.50
TiO_2	---	2.95	---
P_2O_5	---	0.07	---
L.O.I	2.5	9.45	1.18

3.2 Mortar Mix Design, Mixture Proportions and Test Parameters

In order to assess both the effect of adding NC as a partial replacement of cement in concrete matrix and the best NC dispersion technique on concrete compressive strength, different mortar mixes were prepared in the lab. At first, standard mortar mixture was prepared according to ES (2421-2006) [42] to determine the standard w/c ratio. After that, 70x70x70 mm mortar cubic samples (6 cubes per each mix) were prepared with variable replacement ratios (5%, 7% and 9%) of NC by weight of cement. Also, the percentage of SP to

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cement weight was adjusted to maintain the same workability for each mix without changing w/c ratio. In order to prepare mortar mixes, three NC dispersion techniques were adopted; 1- Sonicating, 2- Stirring and 3- Sprinkling after Stirring. Compressive strength of mortar cubes was tested according to ASTM C 109 [43] at ages of 7 and 28 days. Mix proportions of different mortar mixtures are shown in table 2.

3.3 Mortar Mixing, Casting and Curing Procedures

SP was added to mixing water and blended until obtaining homogenous solution. 70% of this solution was utilized to disperse NC. Sonicating process of this mix lasted for 10 min. at 40ºC by water bath sonicator. While, stirring process performed for 2 min. by vane motor. Tables 3 and 4 show the specifications of sonicator and vane motor, respectively.

While preparing water-SP-NC solution, cement and fine aggregates were dry mixed for 1 min. in a rotary mixer. The rest of mixing water and SP were gradually added to the dry blend and mixed for additional 1 min. After that, the previously prepared solution, either by sonicating or stirring, was slowly added or manually sprinkled to the mix for 3 min. time period. After one day from casting, samples were de-molded and cured in tap water till the age of testing.

3.4 Concrete Mixture Proportions and Test Parameters

In order to determine the optimum ratio of NC and MP in the part two of the experimental program, six concrete mixes modified with different ratios of hybrid additions of NC and MP were tested in compression and compared to NSC. NC as cement replacement and MP as sand replacement formed the hybrid addition. The replacement ratios were 3% and 5% for NC, and 5%, 10% and 15% for MP. Variable percentages of SP to cement weight was used to maintain the same workability while fixing w/c ratio for all mixes.

Part three of the experimental program study the effect of the optimum percentages for hybrid additives (3%NC&10%MP) that reported from part two, on mechanical and physical concrete properties of both NSC and HSC.

Mixing proportions of NSC and HSC mixtures with and without hybrid additions for part two and three are shown in table 5. The utilized test standards, specimen dimensions and age of testing are shown in table 6.

3.5 Concrete Mixing, Casting and Curing Procedures

Sprinkling after stirring for NC revealed their efficiency as practical dispersion technique in mortar mixes, thus, the same procedure was applied in concrete mixes. Cement, aggregates and MP were dry mixed in a rotary mixer for 1 min in case of NSC. In case of HSC, SF was also dry mixed with the aforementioned mix. The remaining of the mixing water and SP were added and mixed to the previous blend for 1 min. The ready stirred liquid was manually sprinkled during mixing into rotary mixer for additional 3 min. to achieve the desired homogeneity. After one day from casting, samples were de-molded and cured in tap water till the age of testing.

Table 2. Mixing Proportions of Mortar Mixtures for Part One.

Mix	Mix type	Dispersion Technique	Cement (Kg/m³)	Sand (Kg/m³)	Water (L/m³)	SP (L/m³)	NC (Kg/m³)	Water /binder
M1	Control	--	515	1545	205	10.3	---	0.398
M2	5%NC	Sonicating	489.25	1545	205	12.9	25.75	0.398
M3	7%NC		478.95	1545	205	12.9	36.05	0.398
M4	9%NC		468.65	1545	205	12.9	46.35	0.398
M5	5%NC	Stirring	489.25	1545	205	12.9	25.75	0.398
M6	7%NC		478.95	1545	205	12.9	36.05	0.398
M7	9%NC		468.65	1545	205	12.9	46.35	0.398
M8	5%NC	Sprinkling after Stirring	489.25	1545	205	12.9	25.75	0.398
M9	7%NC		478.95	1545	205	12.9	36.05	0.398
M10	9%NC		468.65	1545	205	12.9	46.35	0.398

Table 3. Specifications of Water Bath Sonicator.

Volume (L)	6
Power supply (V)	220
Frequency (Hz)	50
Power consumption (watt)	200
Timer (Minute)	1-30

Table 4. Specifications of Vane Motor.

Speed range (rpm)	1500-2800
Frequency (Hz)	50
Power consumption (watt)	600

Table 5. Mixing proportions of Concrete Blends for Part Two & Three.

Parts	Mix	Mix type	Cement (Kg/m³)	Sand (Kg/m³)	Agg. (Kg/m³)	Water (L/m³)	SP (L/m³)	NC (Kg/m³)	MP (Kg/m³)	SF (Kg/m³)	Water /binder
Part Two for NSC	M1	C-N	350	780	1150	160	5.25	---	---	---	0.457
	M2	3%NC,5%MP-N	339.5	741	1150	160	5.25	10.5	39	---	0.457
	M3	5%NC,5%MP-N	332.5	741	1150	160	5.25	17.5	39	---	0.457
	M4	3%NC,10%MP-N	339.5	702	1150	160	6.13	10.5	78	---	0.457
	M5	5%NC,10%MP-N	332.5	702	1150	160	6.13	17.5	78	---	0.457
	M6	3%NC,15%MP-N	339.5	663	1150	160	7	10.5	117	---	0.457

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	M7	5%NC,15%MP-N	332.5	663	1150	160	7	17.5	117	---	0.457
Part Three for NSC & HSC	M1	C-N	350	780	1150	160	5.25	---	---	---	0.457
	M4	3%NC,10%MP-N	339.5	702	1150	160	6.13	10.5	78	---	0.457
	M8	C-H	405	720	1145	145	10.35	---	---	45	0.32
	M9	3%NC,10%MP-H	391.5	648	1145	145	11.25	13.5	72	45	0.32

Table 6. Testing standards, specimen dimensions and age of testing.

Test	Standard	Specimen dimensions	Age of testing
Compressive strength	BS EN 12390-3 [44]	150x150x150 mm cube	7, 14, 28 and 90 days
Flexure strength	ASTM C293 [45]	100x100x500 mm prism	7, and 28 days
Splitting strength	ASTM C496 [46]	150x300 mm cylinder	28 days
Bond strength	ASTM C234-91[a] [47]	150x150x150 mm Cube &16 mm deformed steel bar	28 days
Stress & Strain	ASTM C469 [48]	150x300 mm cylinder	28 days
Permeability (Depth of Water Penetration)	BS EN 12390-8 [49]	150x150 mm cylinder	28 days

[a] ASTM C 234-91 was withdrawal and results obtained were used only for comparison.

3.6 Microstructure Methodologies

The microstructure of cement pastes incorporating the optimum ratios of NC and MP that improved NSC, in addition to SF in case of HSC were studied by SEM and TGA to verify the hardened concrete microstructure. The sample used in SEM analysis is a broken piece from a hardened cement paste cube after 28 days. While TGA sample was powder obtained by grounding a broken piece of a tested cement paste cube in compression after 28 days. Mixing proportions of cement paste mixtures are shown in table 7.

4. Analysis and Discussion of Test Results

4.1 Results of experimental work- Part one: Compressive strength of mortar mixtures

The cube compressive strength (f_{cu}) results at 7 and 28 days of mortar containing different NC ratios that dispersed with various techniques are shown in Table 8. Also, Figs. 6 and 7 show the development of compressive strength of different NC mortar mixes, prepared with different dispersion techniques, compared to the control mix at 7 and 28 days. Generally, it was observed that the optimum ratio for NC, regardless dispersion technique, was 5% which enhanced fc at 7 and 28 days. However, increasing NC ratio in mortar over 5% led to less enhancement in fc at 7 days, while, diminished f_c at 28 days for all dispersion techniques. For mortar mixes with 5% NC partial replacement of cement, the enhancement in f_c compared to the reference mix, at 7 days, reached 15.86%, 13.03% and 29.63% for sonicating, stirring and sprinkling after stirring techniques, respectively. While, these ratios increased to 18.29%, 15.02% and 31.31% at 28 days, respectively.

The improvement in f_c can be attributed to two mechanisms; 1- the efficiency of NC in packing the voids by promoting pozzolanic reaction that formed additional C-S-H by consuming calcium hydroxide crystals, 2- the filling effect of NC that strengthened cement matrix and the transition zone surrounding aggregate [12,23,30,36]. While, the decrease in f_c of the mixes beyond the optimum ratio of NC can be attributed to the increase in its surface area which produces more attractive forces between these particles forming weak clogs. These weak clogs fill the pores of the concrete mixture, and consequently, lead to forming weaker hardened matrix. Moreover, the increase in surface area of NC particles leads to difficulties in the hydration process due to the insufficient amount of mixing water to coat all NC particles [30,33].

Sprinkling after stirring technique was more effective compared to individual sonicating or stirring technique. This means that NC agglomeration potential can be successfully eliminated using this technique. Moreover, this technique is practical and can shift the use of NC from research area to industry. Concisely, at all ages, 5%NC addition using sprinkling after stirring technique in mixture led to obtain the highest compressive strength compared to using other dispersion techniques.

Table 7. Mixing Proportions of Cement Paste Mixtures for the Microstructure Analysis.

Mix	Mix type	Cement (Kg/m^3)	Water (L/m^3)	SP (L/m^3)	NC (Kg/m^3)	MP (Kg/m^3)	SF (Kg/m^3)	Water /binder
M1	Control-P	2250	450	22.5	---	---	---	0.2
M2	3%NC,10%MP-P	2182.5	450	30	67.5	225	---	0.2
M3	3%NC,10%MP,10%SF-P	1957.5	450	38	67.5	225	225	0.2

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Table 8. Compressive Strength Test Results of Mortar Mixes.

Mix	Mix Type	NC Dispersion Technique	Compressive Strength (f_c) (MPa)			
			(f_c) 7 days	%Increase in (f_c)	(f_c) 28 days	%Increase in (f_c)
M1	Control	Control	29.7	Ref	44.55	Ref
M2	5%NC	Sonicating	34.41	15.86%	52.7	18.29%
M3	7%NC		32.41	9.12%	38.16	-14.34%
M4	9%NC		31.62	6.46%	37.31	-16.25%
M5	5%NC	Stirring	33.57	13.03%	51.24	15.02%
M6	7%NC		27.9	-6.06%	37	-16.95%
M7	9%NC		26.5	-10.77%	35.1	-21.21%
M8	5%NC	Sprinkling after Stirring	38.5	29.63%	58.5	31.31%
M9	7%NC		33.2	11.78%	39.8	-10.66%
M10	9%NC		32	7.74%	38	-14.70%

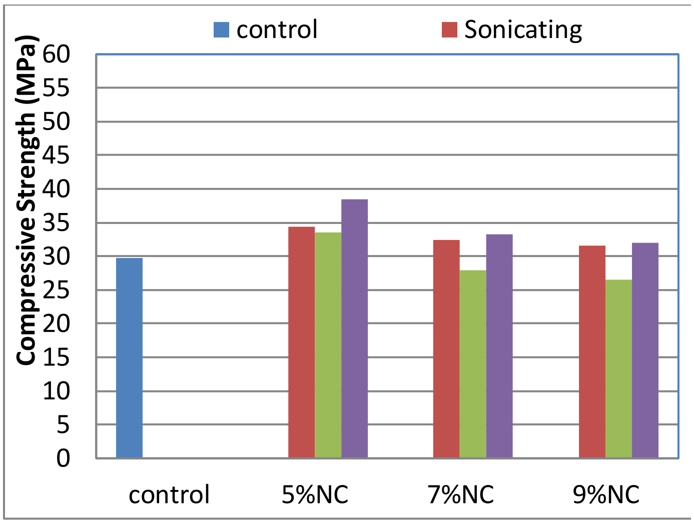

Fig. 6. Compressive Strength of Mortar Mixes at 7 days.

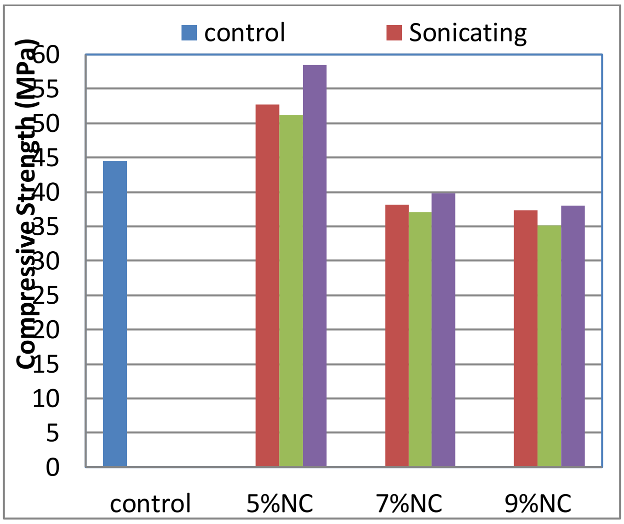

Fig. 7. Compressive Strength of Mortar Mixes at 28 days.

4.2 Results of experimental work- Part two: Compressive Strength of NSC mixtures

The cube compressive strength test results of concrete with different percentages of NC and MP additives are shown in Table 9 and Fig. 8. It is observed that, in all mixes containing different ratios of hybrid additions, the f_c increased compared to control mix (C-N) at all ages. The optimum percentages for hybrid additions were 3% of NC and 10% of MP (3%NC,10%MP-N). The improved percentages of f_c reached about 30% for all test ages.

It can be noticed that the optimum NC ratio as a partial replacement of cement decreased from 5% to 3% in the presence of MP as a partial replacement of sand. This can be attributed to the filling effect of NC transferred to MP. Subsequently NC act as pozzolanic material only by participation in the hydration process of cement.

4.3 Results of experimental work- Part three: Mechanical Properties of Concrete Mixtures

To study the effect of the optimum percentages for hybrid additives that reported from part two, on mechanical concrete properties of both NSC and HSC, four concrete mixes were performed. The mechanical properties of both NSC and HSC with and without hybrid additives are shown in Table 10.

Table 9. Compressive Strength Test Results of NSC Samples.

Mix	Mix Type	Compressive Strength (f_c) (MPa)					
		(f_c) 7 days	%Increase in (f_c)	(f_c) 14 days	%Increase in (f_c)	(f_c) 28 days	%Increase in (f_c)
M1	C-N	29.75	Ref	36	Ref	38.7	Ref
M2	3%NC,5%MP-N	35.4	19%	42.4	17.8%	46.8	20.9%
M3	5%NC,5%MP-N	37	24.4%	44.4	23.3%	47.6	23%
M4	3%NC,10%MP-N	38.4	29.1%	46.9	30.3%	50.4	30.2%
M5	5%NC,10%MP-N	36.6	23%	44.15	22.6%	47.5	22.7%
M6	3%NC,15%MP-N	35.6	19.7%	42.8	18.9%	46.5	20.2%
M7	5%NC,15%MP-N	35.1	18%	42.2	17.2%	45.8	18.3%

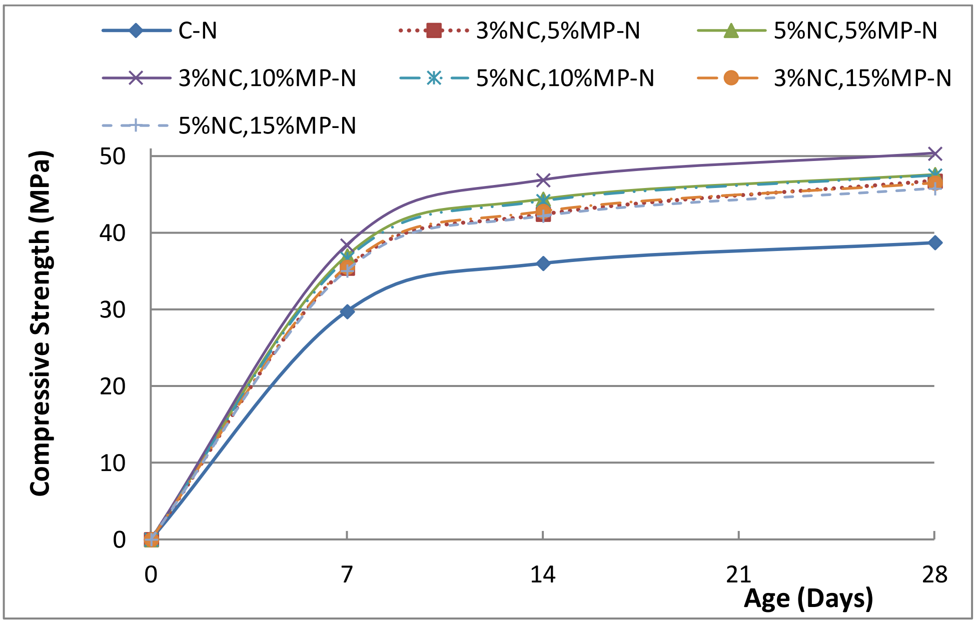

Fig. 8 Development of Compressive Strength of NSC Specimens at Different Ages of Curing.

Table 10. Mechanical Properties of NSC and HSC Samples.

Mix	Mix Type	Test Results (MPa)											
		Compressive strength (f_c)				Flexure strength (f_{ft})				Splitting strength (f_{st})		Bond strength (f_b)	
		7 days	14 days	28 days	90 days	7days	28days	(f_{ft}/f_c) % 7 days	(f_{ft}/f_c) % 28days	28 days	(f_{st}/f_c) %	28 days	(f_b/f_c) %
M1	C-N	29.8	36	38.7	40.7	6.2	7.5	20.8	19.4	3.5	9.0	8.7	22.4
M4	3%NC,10%MP-N	38.4	46.9	50.4	52.5	7.4	9.1	19.3	18.1	4.1	8.1	10.5	20.7
M8	C-H	43	52	57	59.1	8.3	10.3	19.2	17.9	4.5	7.9	11.4	19.9
M9	3%NC,10%MP -H	54.1	65.6	71.7	73.7	9.8	12.4	18.2	17.3	5.2	7.3	13.6	19

4.3.1 Concrete Compressive Strength

Table 10 and Fig. 9 show the development of f_c for NSC and HSC control and optimum mixes. The same trend of improvement by using these additives ratios in HSC was noticed. The improved percentages of fc, compared to HSC reference mix (C-H), reached the range of 25% for all test dates. Moreover, it was observed that f_c of NSC specimens (3%NC,10%MP-N) almost approach the strength of control specimens for HSC (i.e., C-H) that indicated a significant improvement for NSC mixture.

4.3.2 Flexural Strength

The Flexural Strength (f_{ft}) of NSC and HSC control and optimum mixes is given in Table 10 and Fig. 10. For NSC, the improved percentages of f_{ft} to f_c reached about 19.4% and 21.3% at 7 and 28 days, respectively, while for HSC, the improved percentages of f_{ft} to f_c reached 19% and 20.5% at 7 and 28 days, respectively. Briefly, f_{ft}/f_c ratio falls nearly in the 20% range for all NSC and HSC samples. The improvement in the f_{ft} can be attributed to the bridging effect of sheet-like NC particles which strengthened the cement matrix by preventing crack propagation by connecting the both sides of tensile cracks [30,50]. This performance could be observed lately in the SEM micrographs.

Table 10 and Fig. 11 show that the presence of NC and MP in concrete samples decreased the ratio of f_{ft}/f_c in both NSC and HSC samples. This indicated formation of denser and well compacted matrix and led to the increase of brittleness of concrete [51]. **4.3.3 Splitting Strength**

Splitting Strength (f_{st}) of concrete samples appeared to follow the same trend of f_{ft}. Table 10 and Fig. 12 show that the existence of NC and MP in concrete samples improve f_{st} of optimum mixes compared to control NSC and HSC samples. The improved percentages of f_{st} at 28 days compared to control samples reached about 17.1% and 16.2% at 28 days in case of NSC and HSC, respectively.

The ratio of f_{st}/f_c at 28 days of curing are presented in Table 10 and Fig. 13. It can be observed that the average ratio of f_{st}/f_c falls in the range of about 8% for all concrete samples.

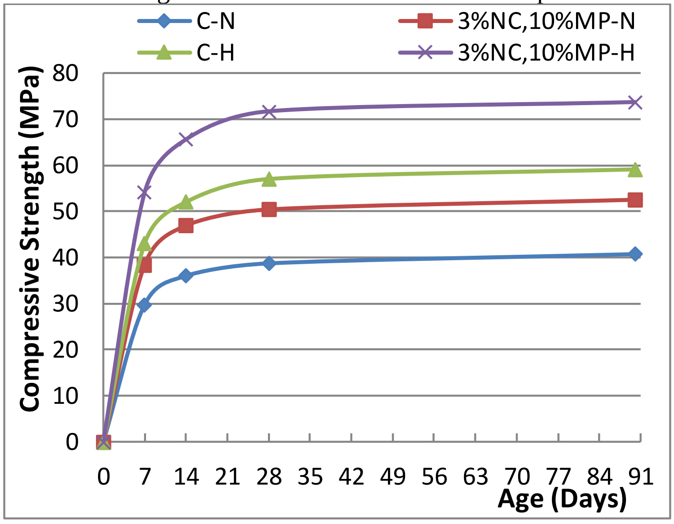

Fig. 9 Development of Compressive Strength of NSC and HSC Specimens at Different Ages of Curing.

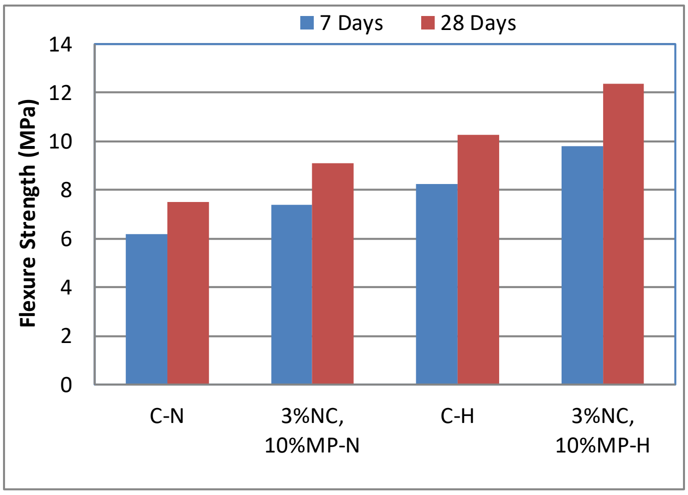

Fig. 10. Flexure Strength Test Results of NSC and HSC Specimens.

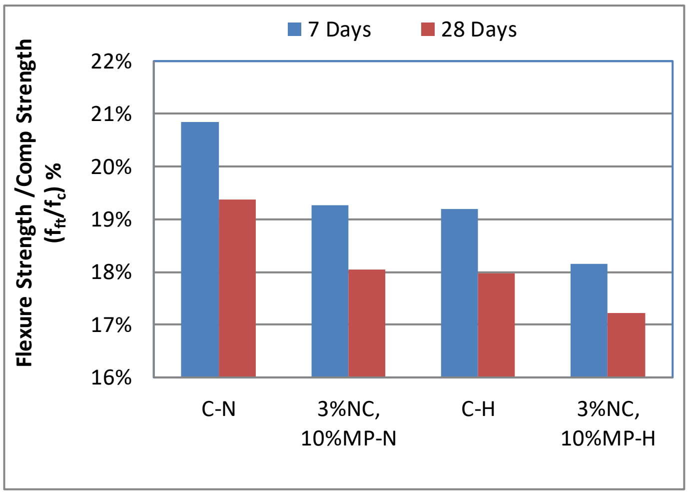

Fig. 11. The Percent Ratio of Flexure Strength to Compressive Strength for NSC and HSC Samples.

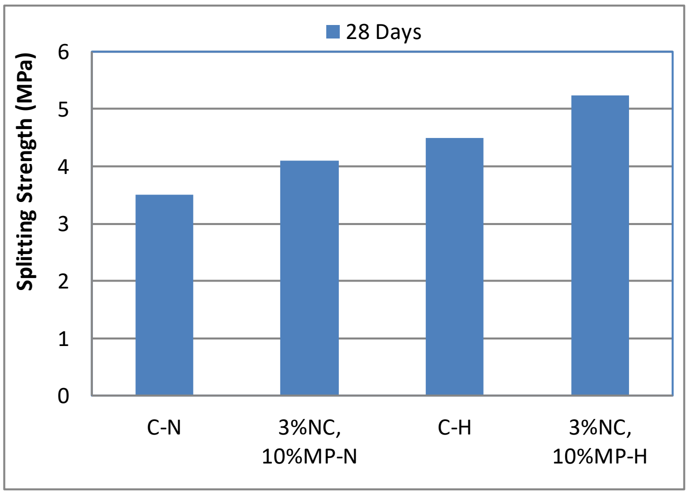

Fig. 12. Splitting Strength Test Results of NSC and HSC Specimens.

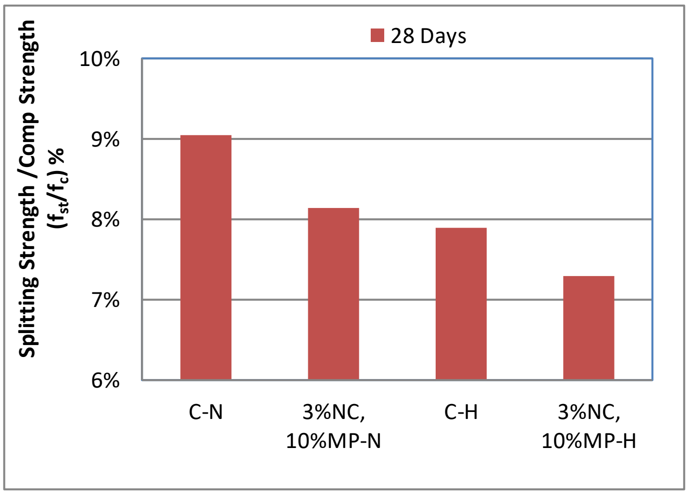

Fig. 13. The Percent Ratio of Splitting Strength to Compressive Strength for NSC and HSC Samples.

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4.3.4 Bond Strength

Table 10 and Fig. 14 show the bond strength (f_b) results at 28 days between steel reinforcement and concrete samples. It is clear that f_b enhanced in optimum samples compared to control samples. The percentages of increase in f_b at 28 days was 20.8% and 19.8% in case of NSC and HSC samples, respectively. Also, Table 10 & Fig. 15 show that the ratio of f_b / f_c is in the range of about 20% for all specimens.

4.3.5 Stress Strain Behavior

The stress strain behavior of NSC and HSC control and optimum mixes are shown in Fig. 16 after 28 days of curing. The ultimate stress, peak strain, elastic modulus, resilience modulus and toughness modulus are shown in Table 11. It is clear that, the elasticity modulus and peak strain of optimum mixes increased slightly compared to control mixes. The percentages of increase in elasticity modulus was 10% and 11% in case of NSC and HSC samples, respectively. Furthermore, the resilience and toughness modulus of optimum mixes increased compared to control mixes. The improved percentages of resilience modulus reached about 26% and 24.4% in case of NSC and HSC samples, respectively, and for toughness modulus reached about 13.4% and 17% in case of NSC and HSC samples, respectively. It is clear that, the improvements in ultimate stress from cylinder compressive strength of control and optimum mixes appeared to follow the same trend of cube compressive strength which previously discussed. It can be observed that, hybrid additions form dense and well compacted matrix which led to increase brittleness of concrete [51].

4.4 Results of experimental work- Part three: Physical Properties of Concrete Mixtures

4.4.1 Permeability

Water permeability test results of specimens at 28 days are shown in Fig. 17. It can be observed that optimum mixes have lower water penetration depths compared to NSC and HSC samples. The decrease in water permeability of optimum samples compared to control samples at 28 days was 29.8% and 28.6% in case of NSC and HSC, respectively. The improvement in resistance to water permeability is attributed to the filler effect of NC and MP, as they reduce the permeable pores in concrete and produce more durable concrete.

4.5 Microstructure analysis

4.5.1 Scanning Electron Microscope analysis (SEM)

SEM analysis was applied to assess the performance of mineral additions in the cement microstructure. SEM micrographs in Fig. 18-20 show scans of the control cement paste, and pastes contain optimum ratios of NC and MP after 28 days of curing. SEM analyses were compatible with the mechanical properties previously discussed. For instance, weaker performance in mechanical properties was noticed for control mixes in comparison to optimum strength mixes. This can be comprehended from Fig. 18 by the presence of ettringite needles, calcium hydroxide crystals (CH) and voids leading to a loose structure. In addition, discontinued calcium silicate hydrate C-S-H plates were also identified.

The optimum presence of hybrid NC and MP in the cement paste matrix either SF was added or not, improved the consistency and the homogeneity of the matrix leading to more compact structure (see Fig. 19). The enhanced mechanical properties of the optimum mixture were confirmed by SEM micrographs. This can be attributed to the filling effect of NC, MP and SF which led to significant decrease of voids ratio in the matrix. Furthermore, the pozzolanic feature of NC and SF enabled the reaction with the remaining calcium hydroxide that produced from cement hydration forming more concentrations of C-S-H in the mixture.

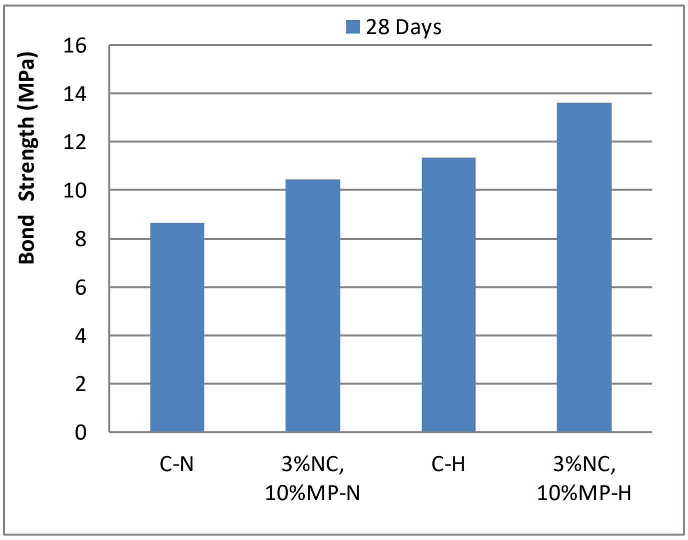

Fig. 14. Bond Strength Test Results of NSC and HSC Samples.

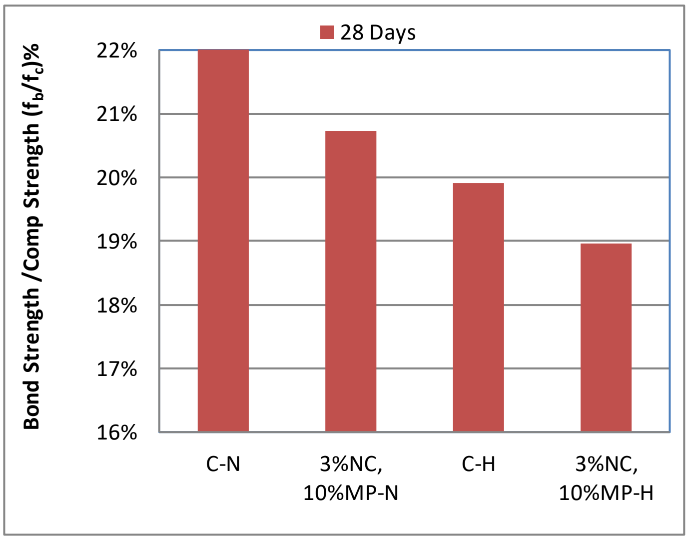

Fig. 15. The Percent Ratio of Bond Strength to Compressive Strength for NSC and HSC Samples.

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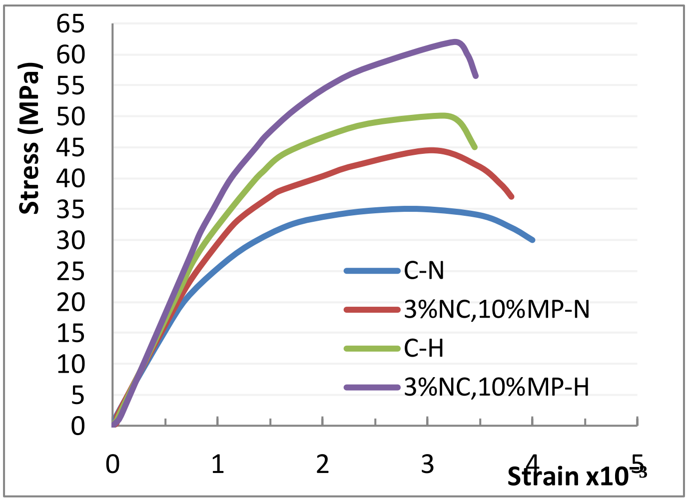

Fig. 16. Stress strain curves of NSC and HSC Samples.

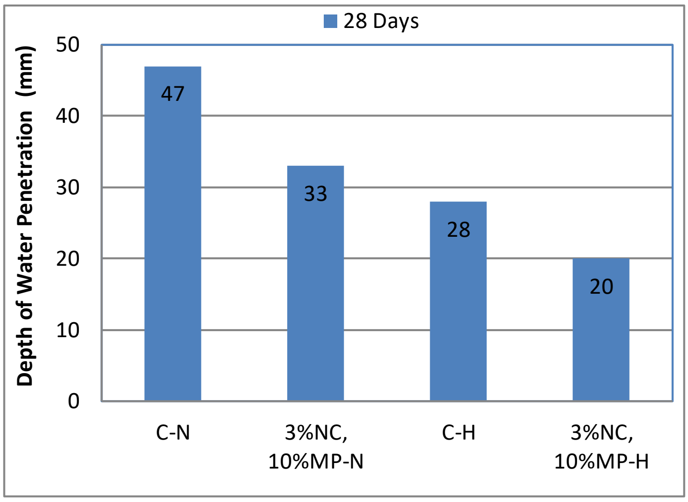

Fig. 17. Depth of Water Penetration Results of NSC and HSC Samples.

Table 11. The ultimate stress, peak strain, elastic modulus, resilience modulus and toughness modulus of NSC and HSC Samples.

Mix	Mix Type	Ultimate Stress (MPa)	Peak Strain (10^{-3})	Elasticity Modulus (GPa)	Resilience Modulus (J/m^3)	Toughness Modulus (J/m^3)
M1	C-N	35	2.96	28.2	7900	112605.5
M4	3%NC,10%MP-N	44.5	3.04	31	9960	127707.5
M8	C-H	50.1	3.15	34.2	13500	128278
M9	3%NC,10%MP-H	62	3.25	38.1	16800	150795

4.5 Microstructure analysis

4.5.1 Scanning Electron Microscope analysis (SEM)

SEM analysis was applied to assess the performance of mineral additions in the cement microstructure. SEM micrographs in Fig. 18-20 show scans of the control cement paste, and pastes contain optimum ratios of NC and MP after 28 days of curing. SEM analyses were compatible with the mechanical properties previously discussed. For instance, weaker performance in mechanical properties was noticed for control mixes in comparison to optimum strength mixes. This can be comprehended from Fig. 18 by the presence of ettringite needles, calcium hydroxide crystals (CH) and voids leading to a loose structure. In addition, discontinued calcium silicate hydrate C-S-H plates were also identified.

The optimum presence of hybrid NC and MP in the cement paste matrix either SF was added or not, improved the consistency and the homogeneity of the matrix leading to more compact structure (see Fig. 19). The enhanced mechanical properties of the optimum mixture were confirmed by SEM micrographs. This can be attributed to the filling effect of NC, MP and SF which led to significant decrease of voids ratio in the matrix. Furthermore, the pozzolanic feature of NC and SF enabled the reaction with the remaining calcium hydroxide that produced from cement hydration forming more concentrations of C-S-H in the mixture.

The pozzolanic activity of the matrix boosted due to silicate mineral which is the main component of NC particles appearing in shape of sheets. Also, the sheets act as bridge connecting both sides of the crack together preventing crack propagation as shown in Fig. 20 [30]. This interpreted the enhanced tensile properties of the optimum concrete mixes. Moreover, the applied dispersion technique, sprinkling after stirring, was efficient to avoid agglomerations of NC as they were not detected in SEM micrographs.

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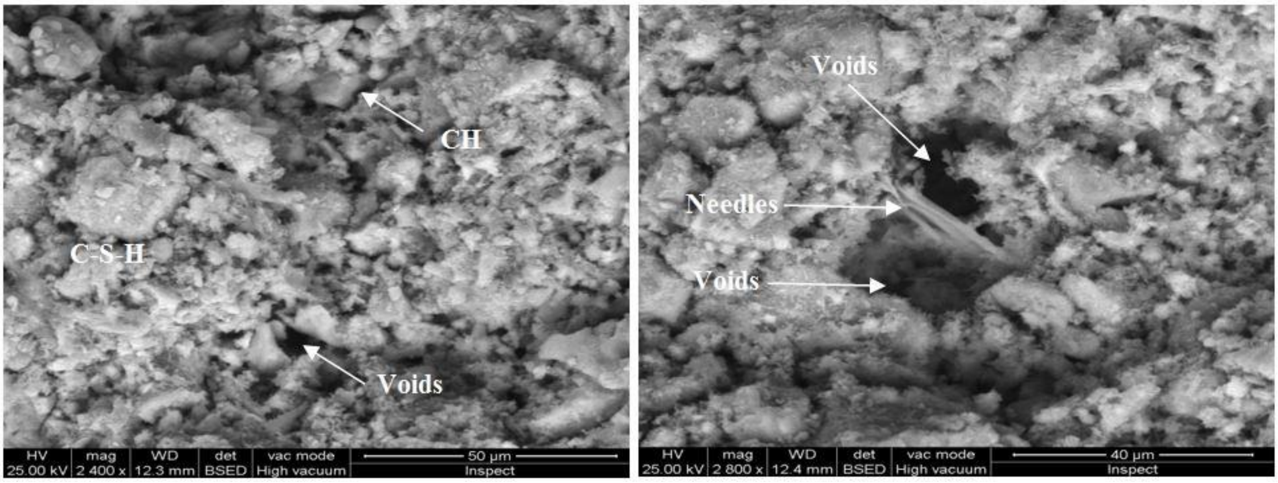
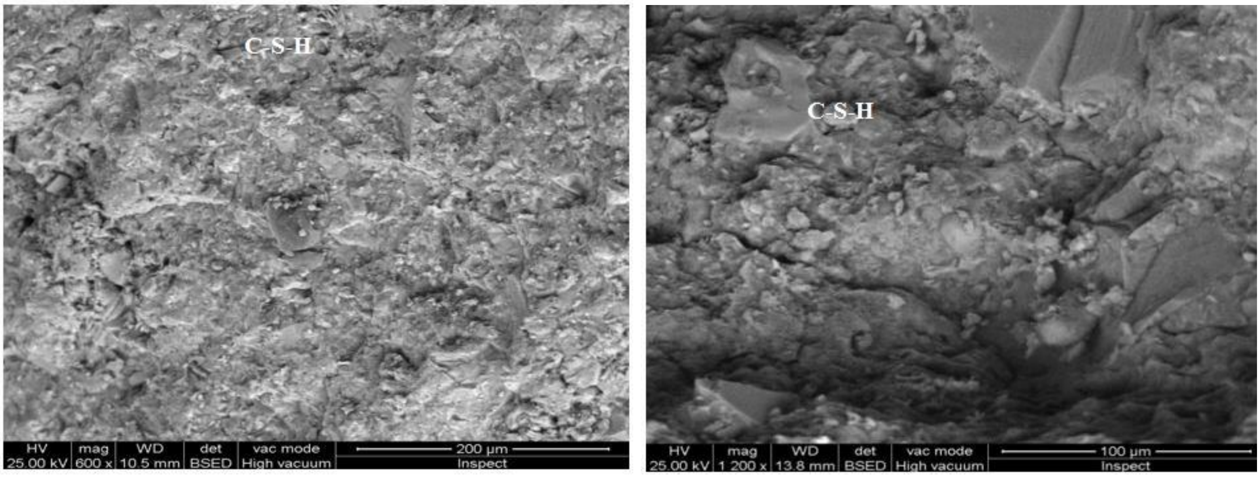
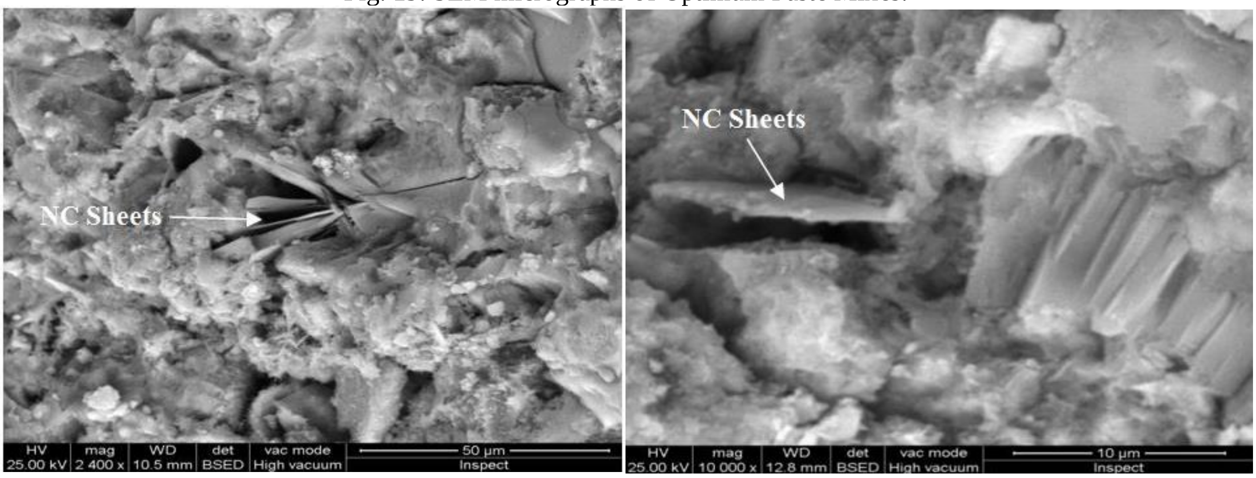


Fig. 18. SEM Micrographs of Control Mix at Two Different Spots.



a) 3%NC,10%MP-P mix **b)** 3%NC,10%MP,10%SF-P mix

Fig. 19. SEM micrographs of Optimum Paste Mixes.



a) 3%NC,10%MP-P mix **b)** 3%NC,10%MP,10%SF-P mix

Fig. 20. Bridge Effect of NC Sheets in Optimum Paste Mixes.

4.5.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a quantitative measurement that records the change in specimen weight, caused by dehydration, decomposition and oxidation of its material at heating range from 20 up to 1000 ºC and rate 10 ºC/min. TGA analysis was applied to assess the effect of mineral additions on the microstructure of paste matrix, and to track the changes in its hydration phases. TGA profiles in Fig. 21 show the percentage weight loss at various temperature range for control cement paste, and optimum cement pastes after 28 days of curing.

From TGA graph, three zones of endothermic peaks were observed. The first zone ranging around 150-250 ºC, indicated the decomposition of C-S-H and ettringite. The second ranging around 415-475 ºC, indicated the decomposition of CH. The third ranging around 750 ºC, indicated the decomposition of calcium carbonate (CaCO3) that was derived from the cement clinker [52]. The first and second zones are indicators to assess the degree of hydration of cement matrix. The CH% content of cement pastes that presented in Fig. 21 was obtained according to the following equation:

CH% = WLCH (%) x (MWCH/MWH2O) [53]

Where, WLCH: the percent weight loss of CH, MWCH: the molecular weight of CH and MWH2O: the molecular weight of H2O.

CH% content for mixes containing pozzolanic additions (NC, SF) is lower than control mix as shown in Fig. 22. This confirms the efficiency of NC and SF in the first and second zones by promoting pozzolanic reaction that formed additional C-S-H by consuming CH crystals. For the effect of MP addition, weight loss drops obviously in the third zone for mixes containing MP indicating the higher content of $CaCO_3$ confirming the filling role of MP rather than participation in the hydration process of cement. TGA observations confirm the interpretations in the mechanical/physical test results and compatible with [12,14].

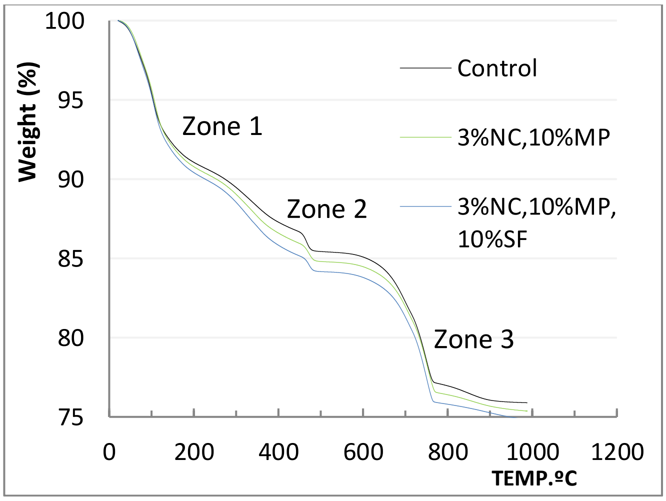


Fig.21 TGA curves for different cement pastes after 28 days of curing.

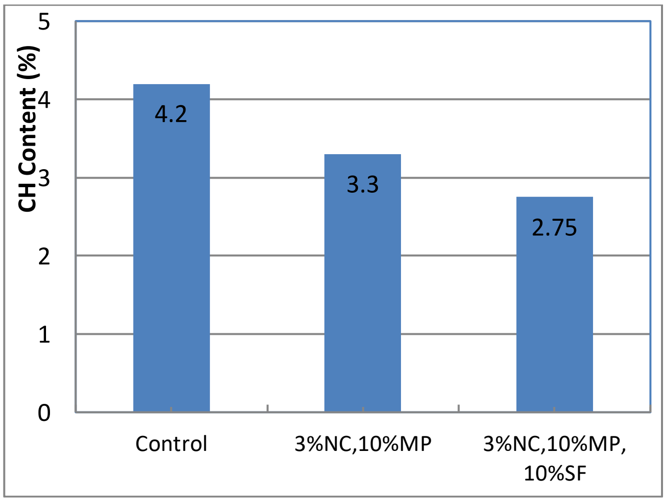


Fig.22 CH content (%) for different cement pastes after 28 days of curing.

5. CONCLUSIONS

Based on the experimental results shown in this study the following conclusions were obtained:

1. Sprinkling after stirring dispersion technique represents an effective and practical mean to overcome NC agglomeration problem in concrete mixes.
2. Using different ratios of hybrid additions as NC (as cement replacement) and MP (as sand replacement) in normal strength concrete enhanced the compressive strength. The optimum percentages of hybrid additions were 3% of NC with 10% of MP.
3. Using different ratios of waste MP as partial hybrid addition to NC was effective in reducing the ratio of NC in concrete mixture resulting in optimum percentage of NC of 3% instead of 5%. Consequently, this facilitated nanoparticles dispersion in the mixture, minimized the cost of the mixture and had a good impact on the environment.
4. Nano clay particles improve the features of the mixtures by packing the voids, promoting pozzolanic reaction, and forming additional C-S-H by consuming calcium hydroxide crystals. This was achieved by using suitable dispersion techniques.
5. MP packs the voids in concrete mixture as filler effect that strengthened cement matrix.
6. Hybrid additions as NC and MP improved the mechanical properties at certain percentages. Otherwise, the use of excessive amounts forms weak clogs of these additives as a result of the high surface area or the increased demand in the mixing water amount.
7. Concrete mixtures incorporating the optimum percentages of NC and MP improved the compressive strength compared to normal and high strength concrete. The improved percentages of compressive strength reached 30.2% at 28 days in case of using NSC and 25.8% at 28 days in case of using HSC.
8. Utilizing the optimum percentages of NC and MP positively affected the tensile strength of normal and high strength concrete through flexure and splitting tests.
9. A noticeable improvement in bond strength of normal and high strength concrete was recorded at the optimum percentages of NC and MP.
10. Concrete mixtures incorporating the optimum percentages of NC and MP slightly improved the elasticity modulus compared to normal and high strength concrete. The improved percentage reached about 10% at 28 days in case of using NSC and HSC.
11. The use of the optimum percentages of NC and MP in concrete mixtures produced less permeable concrete resulting in enhanced durability compared to control concrete samples.

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