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The Mechanical Properties, Water Permeability and Microstructure of Cement Mortar Incorporating Nano Clay Particles

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ABSTRACT

In this paper, the strength properties and water permeability of cement mortar containing 1, 3 and 5 wt% of nano clay (NC) particles have been studied and compared to the plain cement mortar. Experimental results have shown that the compressive, tensile, flexural strength and the water permeability of the cement mortar containing 1wt% NC particles have been considerably improved at the 7th day. The scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis have been used to analyze the mechanism of these effects. The results show that the NC particles fill in the voids, reduce the size and amount of calcium hydroxide (CH) and improve their arrangement.

Keywords: *Microstructure, cement, Nano clay*

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INTRODUCTION

Cement-based materials have a vast application in construction. Today, mineral additions such as fly ash and blast furnace slag are being widely used to improve these materials [1, 2]. Partial replacement of cement with mineral additions improves the Cement-based materials; in addition, it reduces both the diffusion of CO2 which is produced during the process of cement production, and the damaging effects on the environment. In this regard, the application of nanoparticles have been vastly increased in the recent years, since due to their small size, they have unique properties such as huge specific surface area and high activity. There are many reports on the effect of nanoparticles addition to the cement-based materials.

Meng and his collaborators [3] have studied the effect of nano-TiO2 on the mechanical properties of cement mortar. Results show that when cement is replaced with TiO2 nanoparticles, the strength of cement mortar is widely increased.

Qing et al [4] have shown that the addition of SiO2 nanoparticles to the hardened cement paste increase the compressive and bonding strength of paste-aggregate interface more than Silica fume addition, which is due to the fact that SiO2 nanoparticles have higher specific surface and larger number of atoms in the surface, so they will have higher chemical reactions.

Arefi et al [5] have studied the effect of the addition of SiO2 particles with different diameters and content to the cement mortar. The results of their studies shows that nanoparticles will improve the strength properties and permeability of cement mortar more than micro particles, since they have higher specific surface area. In addition, by increasing the diameter of SiO2 nanoparticles, the probability of getting agglomerated is reduced and will have better effects on the mechanical properties of cement mortar.

Some studies have been conducted, focusing on the effect of the addition of different nanoparticles and comparing their effects. For example, research studies in which the addition of TiO2 nanoparticles have been compared to SiO2 show that the abrasion resistance and flexural fatigue of concrete including TiO2 nanoparticles is more than the abrasion of the concrete including the same amount of SiO2 nanoparticles [6, 7]. Also, the improvement of resistance to chloride penetration of the concrete containing TiO2 is more than concretes containing the same amount of SiO2 [8]. Recent studies have shown that nanoparticles like Al2O3, Fe2O3 and SiO2 have high reactivity due to their high surface area and act as nuclear in the cement paste and promote pozzolanic reaction [9-11]. In addition, nanoparticles act as fillers and compact the structure of hydrate products [12-14]. Among nanoparticles, NC particles generally have a flat, thin sheet-like crystalline structure, and the thickness of the crystalline layer is about 1 nm while the other dimensions can be up to 1000 nm or more. This high aspect ratio is a very important factor in reinforcing.

There are few reports about the addition of NC particles on cement–based materials. Morsy and his collaborators [15] have shown that the addition of NC particles will improve the microstructure of cement mortar, and will increase the tensile and flexural strength. Alya and his collaborators [16] have studied the effect of NC particles on waste-glass cement mortars. The results of their study show that the mechanical properties of the cement mortars with a hybrid combination of glass powder and NC particle were all higher than those of plain mortar and with glass powder .

Research studies conducted in the past focused more on the strength properties of cement mortar including NC particles. In this study different amounts of NC particles have been used to achieve an optimal amount of NC particles that in addition to high strength properties, it will have appropriate permeability too.

MATERIALS AND METHODS

Portland cement type II conforming to ASTM C150 [17] Standard was used. The chemical and physical properties of the cement are shown in Table 1. The Clay particles were a kind of MMT modified with a ternary ammonium salt, purchased from Southern Clay Products Inc. Its main characteristics are given in Table 2.

The superplasticizer was a commercial sulphonated melamine formaldehyde polymer manufactured by Vand Chemie in Iran with a relative density of 1.15. Since a large content of nanoparticles need more water for the cement paste, in this study, in order to prevent self desiccation by increasing the added nanoparticles, the amount of superplastizer is increased too.

Also, distilled water was used for preparing the mixtures. The utilized aggregate was the crushed silica sand with apparent density of and the fineness modulus of 2.6. The sand was graded according to ASTM C33 [18] standard and the largest diameter of these aggregated particles was up to 4.75mm.

The mixtures were prepared with the cement replacement of 1%, 3% and 5% by weight of cement. The ratio of water to binder (the cement and clay particles) for all mixtures was 0.42. The mixing ratios of the plain cement mortar and the cement mortar containing NC particles are shown in Table 3. Uniform distribution of nanoparticles in cement mortar severely depends on the creation of stable suspension. Kuo et al [19] and Alya et al [16] have successfully used the high speed mix technique for adding the modified montmorillonite to the cement matrix. In this study, such technique has been used.

NC particles were mixed with the distilled water in a magnetic stirring for 10 hours at high rotational speed. Production steps comprised of the following processes.

I. The suspension of the NC particles and the superplasticizer were mixed in the mixer for 30 second.

II. The cement was added to this mixture simultaneously. Thereafter, the sand, from finest to coarsest, was added gradually to the mixture, and the mixing continued until the complete homogenization of the mixture.

Then, the mortar was poured into the standard mold. For tensile test, the briquette specimens with 75×25×25 mm dimension were utilized. The mortar was poured in two layers, both of them compressed by 4 impacts of a steel rod. In order to prepare the specimens of the compressive and water permeability tests, the mortar was poured into molds to form cubes of size 50×50×50 mm in three layers alternatively, which all layers compressed by 10 impacts of a steel rod. In order to prepare the specimens for the flexural test, the mortar was poured into the molds with dimensions of 40×40×160 mm in two layers. Each layer was compacted by 15 impacts of a steel rod. The molded specimens were covered with a plastic sheet for 24 hours and then were cured in water at the room temperature. Testing of the specimens was performed after 7days. Six specimens were prepared for each test and the average result was reported

An apparatus (ELE Company, England) was used for performing the mechanical tests. Flexural test was done in accordance to the ASTM C348 [20]. Compressive tests were carried out according to the ASTM C109 [21] Standard and tensile tests were performed conforming to the ASTM C190 [22] standard.

Having conducted the mechanical tests, the central parts of the crushed specimens were chosen for XRD and SEM tests. A Philips PW-1800 unit was used for XRD analysis. The microstructure of the specimens was studied using the scanning electron microscopy (Hitachi S-4160).

Table 1 Chemical and physical properties of Portland cement (wt %).

Material	SiO2	Al2O3	Fe2O3	CaO	MgO	SO3	Na2O	K2O	L.O.I	I.R
Cement	20.92	4.61	4.16	62.10	2.75	2.02	0.30	0.59	1.40	0.40

Table 2 Properties of modified montmorillonite

Item	Organic modifier	Weight loss on ignition (%)	X-ray results (d001)(Å)	Modifier concentration
Cloisite 30B	MT2EtOH	7	18.5	90 meq/100g clay

*MT2EtOH (methyl, tallow, bis-S-hydroxyethyl, quaternary ammonium)

Table 3 Mix proportion of specimens (kg/m3)

Sample name	Water	Cement	Sand	Nano Clay particles	*SP
*PC	150	360	1800	-	-
1NC	150	356.4	1800	3.6	3.68
3NC	150	349.2	1800	10.8	4.29
5NC	150	342	1800	18	4.9

*PC: plain cement mortar

*SP: superplasticizer

RESULTS AND DISCUSSION

1 MICROSTRUCTURE

In order to study the mechanism that the mechanical properties tests have shown SEM analysis was conducted and it was specified that the addition of NC particles to the cement mortar will affect the hydration process and will cause differences in the microstructure. Figs. 1 and 2 show the microstructure of plain cement mortar. As it is shown in Fig. 1, in the microstructure of plain cement mortar, the C-S-H gel exist in isolation and are joined by needle-like hydrate and large CH crystals that make up a structure with large voids. Fig. 2 shows the arrangement of CH crystals in the plain cement mortar with a more clear resolution. As the figure shows, large CH crystals have a high degree of orientation and their edges of hexagonal plates are clear.

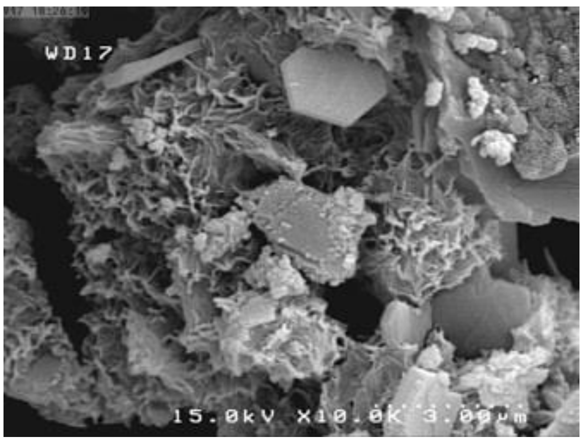


Fig. 1 SEM micrographs of specimen PC

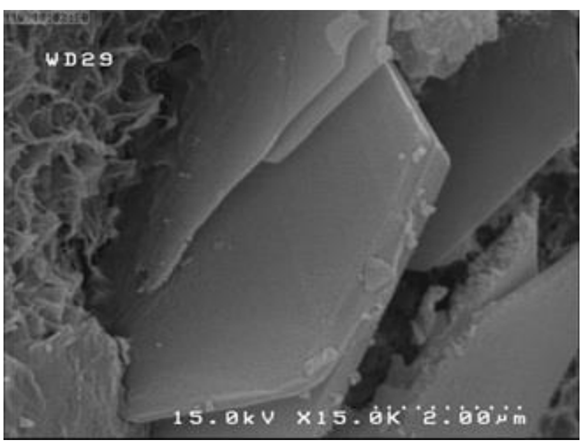


Fig. 2 SEM micrographs of specimen PC

Fig. 3 shows the microstructure of specimen 1NC. It is seen that the microstructure of this specimen are completely different from the microstructure of plain cement mortar, since with the addition of NC particles up to 1% , nanoparticles fill the voids, decreases the content, the size, and the degree of orientation of CH crystals. Also, the edges of CH crystals are eroded and as a result fine crystals fill the voids of C-S-H skeleton, and the structure of hydrate products have become more compact.

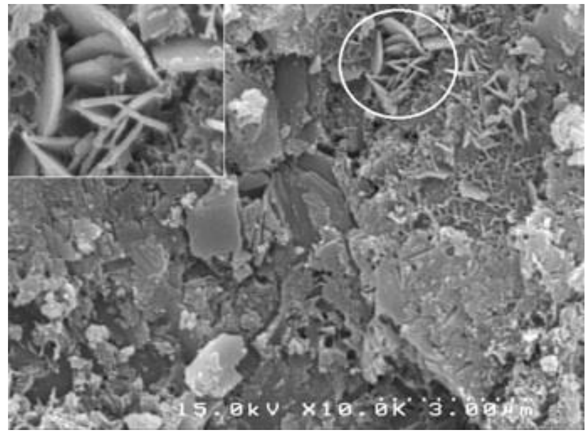


Fig. 3 SEM micrographs of specimen 1NC

The microstructure of specimens 5NC and 3NC have been shown in Figs. 4 and 5. As Fig. 4 shows, the microstructure of specimen 3NC is somehow dense and compared with the microstructure of plain cement mortar, there are less voids, but compared with 1 NC microstructure it has less compact.

In both, the size of CH crystals has decreased compared to the plain cement mortar. The difference, as is shown in Fig. 6, is that in specimen 5NC, micro-cracks are observable. The appearance of these micro-cracks can be explained in this way that the concrete contains solid phases which can shrink or expand (notably C-S-H), inert solid phases such as aggregate, and pores. The presence of inert solid phases ensures that there is some degree of restraint. The effect of shrinkage or expansion of the C-S-H on the pore size will depend on the content of the restraint [23].

During the cement hydration process, C-S-H gel increases. With the increase in the content of NC particles more than the content required to participate in the hydration process will remain in the system and makes an increase in the inert solid phase, and as a result causes a rise in the amount of restraint. As it is shown in Figs. 5 and 6 this causes the growth of voids and the number of micro-cracks.

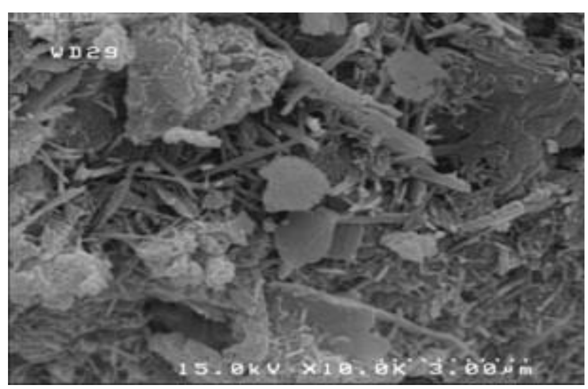


Fig. 4 SEM micrographs of specimen 3NC

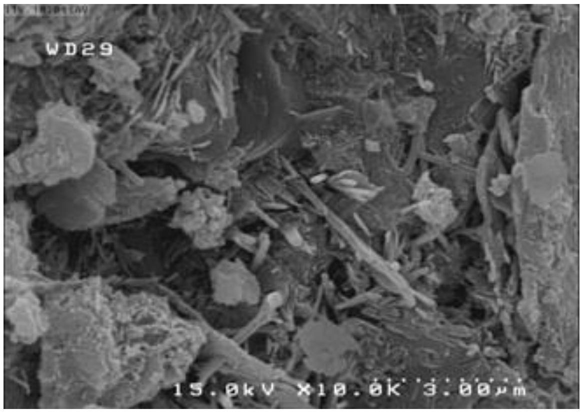


Fig. 5 SEM micrographs of specimen 5NC

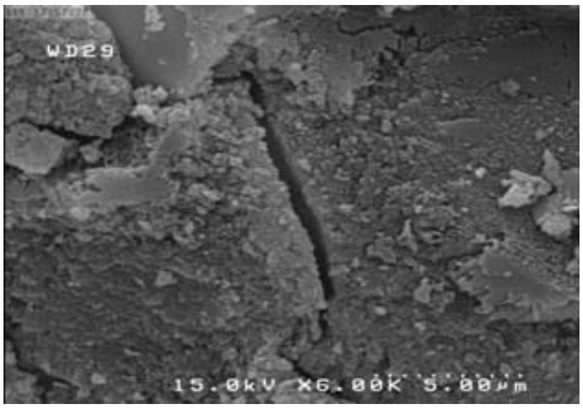


Fig. 6 SEM micrographs of specimen 5NC

The mechanism which makes improvements in the microstructure by adding nanoparticles can be explained as follows. Because of hydration reactions between water and cement, a large number of CH crystals are produced. Large flat CH crystals are formed in interfacial transition zone and between aggregates and binding paste matrix, perpendicular to the surface of aggregate grains, which results in the formation of highly porous structure in the cement paste [24, 25]. When nanoparticles are distributed in the cement paste with a suitable amount, they will prevent the growth of CH crystals and will improve their arrangement and as a result makes the microstructure more dense.

3-2 XRD analysis

The XRD spectrum of the specimens are shown in Fig. 7. The consumption of CH crystals can be demonstrated by intensity changes of diffraction peak of CH crystals at 2 θ =18.12º. The intensity of this peak in the specimens 1NC, 3NC, and 5NC has decreased by 43.8%, 13.85% and 7.7%, respectively, compared with plain cement mortar.

Also, the carbonation process is observable by diffraction peak of CaCo3 at 2ϴ =29.44º which is the main product of carbonation reactions [26]. Compared to the plain cement mortar, in 1NC, 3NC and 5NC specimens, this peak has increased by 14%, 9.7%, and 6.37% respectively.

Qing [4] and Meng [3] used the XRD spectrum for analyzing the orientation index of CH crystals. The diffraction angle 2ϴ of (101) crystal face of CH crystal was 34.04º and that of (001) crystal face was 18.12º. Orientation index (R) of CH crystal can be calculated by R=(1.35×I(001))/ I(101).

The orientation index of specimens PC, 1 NC, 3NC and 5NC are 1.62, 1.13, 1.40 and 1.51 respectively. This shows that by the addition of NC particles, the orientation degree is improved which corresponds with the results of SEM analyses.

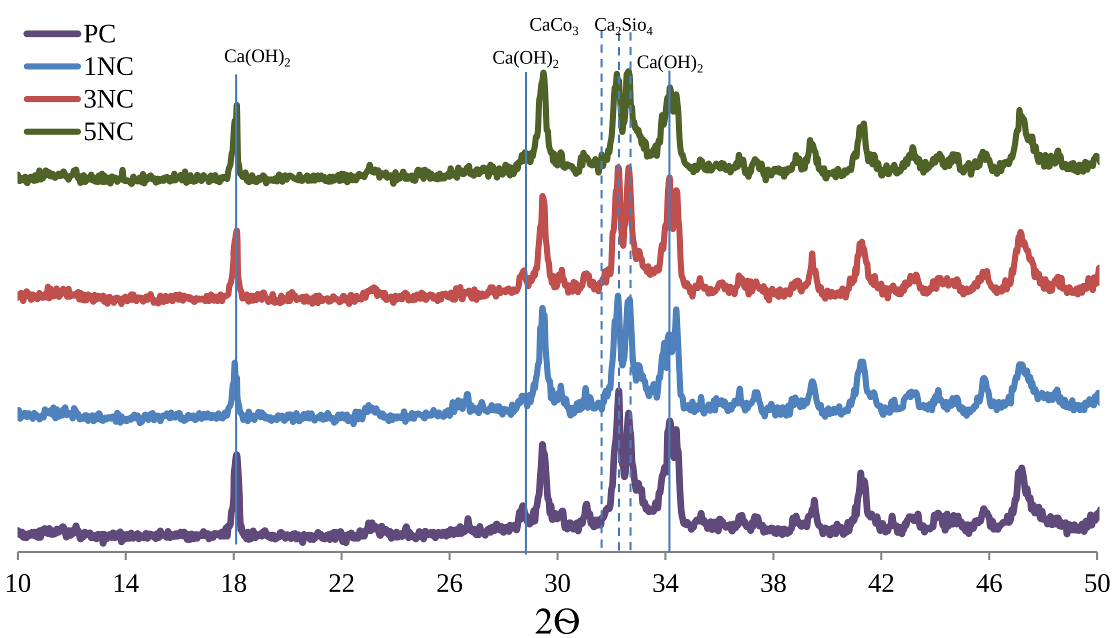


Fig. 7 XRD results of specimens PC, 1NC, 3NC, 5NC

3 MECHANICAL PROPERTIES

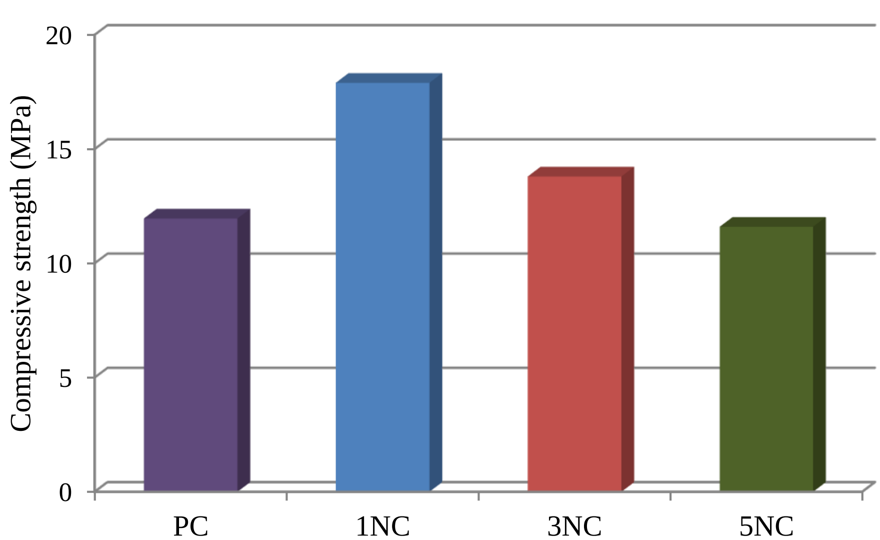
Table 4 and Fig. 8 the results of compressive, tensile and flexural tests of specimens containing NC particles and plain cement mortar are shown. The results show that by the addition of NC particles up to 1% of cement weight, the strength has increased. The mechanism that NC particles increase strength of cement mortar can be justified as follows. The silica existed in NC particles can participate in the hydration process to decrease large CH crystals and accelerates the formation of C-S-H gel. Also SEM and XRD analyses show, they improve the arrangement of CH crystals. On the other hand, the NC particles fill the interstitial spaces inside the C-S-H gel due to their great surface area, which leads to a denser and more compact structure and as a result they increase the strength of cement mortar

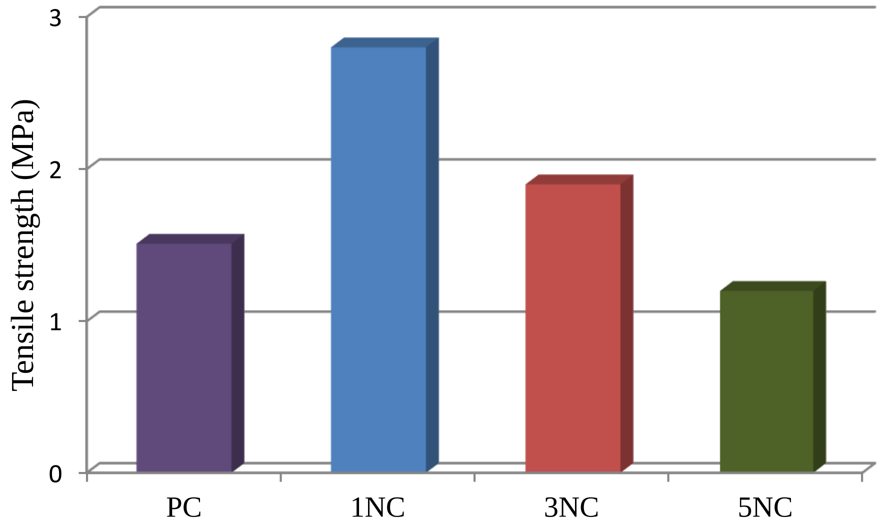
Also, the increase in the diffraction peak intensity of CaCo3 in specimens containing NC particles is the sign of the increase in carbonation process which can cause the reduction of porosity [27] and improvement of cement mortar strength.

In the specimen containing 3wt% of NC particles compared with the specimen containing 1wt% of NC particles the strength will sharply decrease, so that by increasing the content of NC particles up to 5wt % , the strength has even become less than plain cement mortar. This can be due to the fact that by increasing the content of NC particles, they become agglomerated around cement grains leading to partial hydration of cement grains and producing hydrated product having weak bond [28]. On the other hand, by increasing the content of NC particles, the surface interactions of cement matrix and NC particles reduces [29]. It can be noticed from table 4 that with the addition of NC particles, the enhanced extent of tensile and flexural strength in specimens containing 1 and 3wt% of NC particles is more than the enhanced extent of compressive strength. This is because NC particles act like fibers in the cement matrix, due to high aspect ratio and by bridging among micro-cracks, they resist against crack propagation and crack opening. By adding extra amount of NC particles in specimen 5NC, the specific area of binder increases, and consequently the workability of concrete decreases and micro-cracks will increase (fig. 6) whose effect on the tensile and flexural strength will be more than compressive strength [30, 6]. On the other hand, with the reduction of surface interactions of mortar matrix and NC particles, their effect on bridging between cracks is reduced. These two factors has caused that the amount of tensile and flexural reduction in the 5NC be greater than that of compressive strength.

Table 4 Mechanical properties of specimens

Mixture type	Compressive strength		Tensile strength		Flexural strength	
	Value (MPa)	Enhanced extent (%)	Value (MPa)	Enhanced extent (%)	Value (MPa)	Enhanced extent (%)
PC	11.96	-	1.51		2.2	-
1NC	17.9	50	2.8	85.43	3.7	68.18
3NC	13.8	15.38	1.9	25.85	2.7	22.72
5NC	11.6	-3	1.2	-20.52	1.9	-13.64





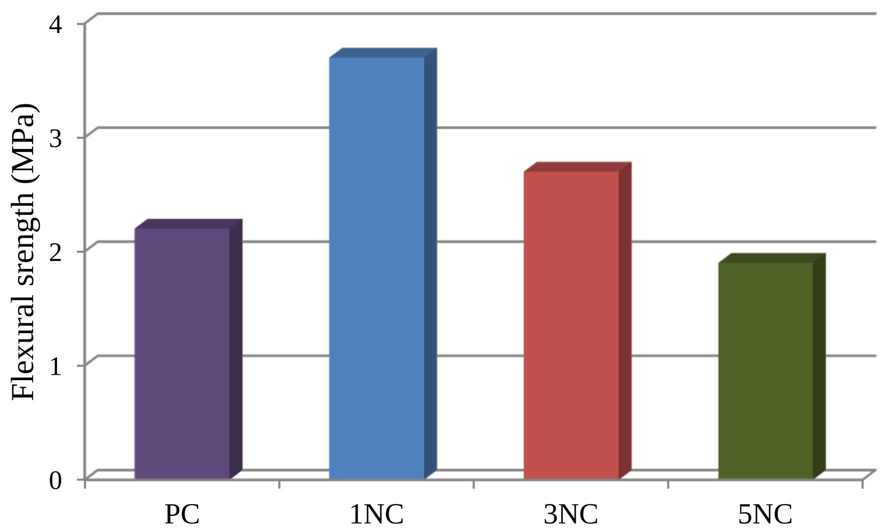


Fig. 8 (a) Compressive strength, (b) Tensile strength, and (c) Flexural strength of specimens

3 WATER PERMEABILIT

Water permeability tests are performed with several methods such as coefficient of water absorption, percentage of water absorption and rate of water absorption [9]. In this study water permeability tests were performed by percentage of water absorption. After demolding the cement mortar, the specimens were cured in water for 5 days, and dried at the ambient atmosphere for 2 days. Then, the specimens were weighed (W_{dry}); thereafter, they were cured into water for other 24 hours, and then weighed again (W_{wet}). The percentage of the water absorption (permeability) was calculated using the following formula:

$$P\% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

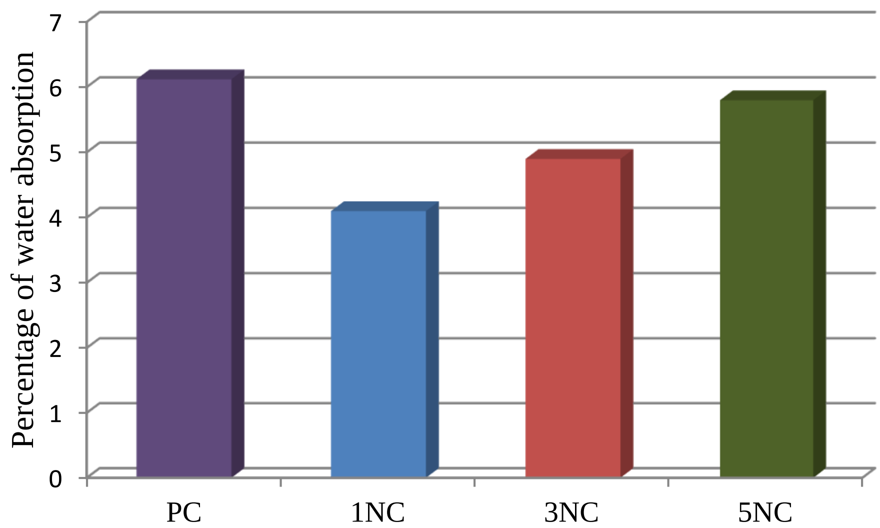


Fig. 9 Percentage of water absorption of specimens

The results are presented in Fig. 9. As seen the highest percentage of water absorption is for plain cement mortar, and the lowest percentage of absorption is related to specimen 1NC were the results are confirmed by SEM images.

In one hand , nanoparticles act as fillers and reduce the permeable voids, and on the other hand, because of their high specific area , they will increase the wettable surface area and as a result, will increase the content of water absorption. As it is shown in SEM figure of specimen 1NC (Fig. 3) the voids are decreased and has caused the least amount of water absorption . However, in the specimens 3NC and 5NC, the increase in both the voids (Figs. 4 and 5) and the wettable surface area has caused the increase of water absorption.

4.Conclusions

In this study, in order to examine the possibility of applying NC particles in cement-based materials, the partial replacement of cement by NC particles (1, 3 and 5wt%) has been tested, and the following conclusions have been drawn :

1. The cement mortar containing 1 and 3 wt% NC particles has a clearly higher strength than plain cement mortar. An optimal amount of 1%wt was gained. However, in specimens containing 5 wt% NC particles, the strengths have become less than plain cement mortar, because of the appearance of micro-cracks.

2. SEM and XRD studies showed that NC particles not only can decrease the content and size of CH crystals but also they can improve the arrangement of CH crystals.

3. Because of high aspect ratio, NC particles act like fibers in the cement matrix, and as a result, they increase the tensile strength more than compressive strength.

4. Due to their great surface area, NC particles act as fillers and reduce the permeable voids. As a result, they improve the water permeability of cement mortar.

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