



Article Enhancement of the Concrete Durability with Hybrid Nano Materials

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Abstract: The importance of the incorporation of nanomaterials in concrete has emerged as a promising research interest due to the outstanding functionalized properties of the materials at that size level. This study aims to investigate the engineering and durability properties of concrete incorporated with hybrid nanomaterials. In this study, the influence of carbon nanotube (CNT) on microstructure, mechanical, and corrosion characteristics of nano-clay-based (NC) concrete has been evaluated. The cement was replaced with CNT at different percentages of 0.01%, 0.02%, and 0.04% by weight, while NC was replaced at a constant percentage of 5%. A scanning electron microscope (SEM) was used to examine the microstructural characterization of the samples. To investigate the influence of carbon nanotubes in the fresh properties, slump and air content tests were carried out. The compressive strength, tensile strength, flexural strength, and bond strength of the hardened concrete was evaluated according to ASTM standards. The porosity of specimens was determined by carrying out the sorptivity and water penetration tests. The corrosion resistance of the steel bar embedded in concrete was assessed. The results of SEM examinations showed that incorporating CNT into the nano-clay-based concrete remarkably achieved a denser structure at all studied contents. Further, significant enhancements in the mechanical properties, durability, and chloride penetration resistance were attained when incorporating CNT in the NC concrete. Further, adding CNTs improves the corrosion resistance and has proven useful resistance to crack propagation within the concrete matrix as compared to the control mix without CNT. Results of this study prove that the incorporation of hybrid nano CNT and NC gives better performance for mechanical strength and durability properties.

Keywords: nanoclay; carbon nanotubes; tensile strength; sorptivity; corrosion; chloride penetration

1. Introduction

Concrete has been vastly used in the construction field because of its high compressive strength, low cost, as well as availability of its raw materials. Its poor resistance to tension stresses makes it quasi-brittle, susceptible to cracking, and undergoes fracture rapidly when the tensile loads are applied. The reinforcing components such as steel bars solve this problem, behaving as a skeleton of the whole structure, and is capable of holding aggregates under tensile loading. The environmental circumstances make the durability of concrete very important when being exposed to aggressive conditions. Generally, after passing 28 days of the curing period, the cementitious paste provides and protects the steel rebar with an alkaline environment by creating a protective ferric oxide film in the high pH environment of concrete. Nevertheless, the presence of carbonation and chloride penetration over the critical concentrations leads to the destruction of the passive film on the steel surface. However, concrete could help in the protection of reinforced steel when being of high pH level, the level that is developed by the cementitious hydrated products especially by the addition of cementitious based supplementary cementitious



Citation: Gamal, H.A.; El-Feky, M.S.; Alharbi, Y.R.; Abadel, A.A.; Kohail, M. Enhancement of the Concrete Durability with Hybrid Nano Materials. *Sustainability* **2021**, *13*, 1373. https://doi.org/10.3390/ su13031373

Academic Editor: Mostafa Ghasemi Baboli Received: 24 December 2020 Accepted: 21 January 2021 Published: 28 January 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). material (SCM) such as silica fume [1], fly ash, slag [2,3], nano-silica, and recently nano clay (NC) [4–7].

Sustainability is considered to be one of the highest and challenging issues in the construction industry [3,8–10]. The high demand for utilizing more sustainable materials turns to the development of nanotechnology [11]. Nanotechnology can lead to utilizing materials with a significant and higher specific area and superior mechanical and durability properties than conventional materials [12–14]. Nanomaterials can be categorized into two groups; pozzolanic nanomaterials (nano alumina, nano silica [14–16], nano clay [17]), and fiber-like nanomaterials (carbon nano-fiber and carbon nanotubes [18]). It was reported that all pozzolanic materials possess high pozzolanic reactions with calcium hydroxide forming additional calcium silicate hydrates gel. This in turn leads to improving the concrete engineering properties [19]. Fiber-like materials are featured by their needle action due to their shapes, which exhibit the bridging effect for the cracks and the prevention of their propagation leading to improvement of the tensile properties of the concrete [7,18,20].

The manufacture heating condition under temperatures of 650–900 °C for 3 h makes the nano clay different from the other mineral supplementary nano-admixtures, where it acts as a highly reactive synthetic pozzolanic nanomaterial due to the formation of anhydratealumino-silicate $(Al_2Si_2O_7)$ and (AS_2) as a mainly formless compound [21]. It was found that the alkaline environment of concrete is developed by pozzolanic reactivity of NC with calcium hydroxide released throughout the hydrated process extra calcium silicate hydrate (C-S-H) that gets deposited in the pore system, hence causing an enhancement of the mechanical properties. Besides that, the NC has a great filling impact, consequently producing denser micro-skeleton and nucleation effect, helping to promote and accelerate the hydration process. The consequence of the transition from passive to active corrosion state causes in generation billions of fine cracks that begin to widen. It was revealed that using nanofibers has a great bridging influence in inhibiting the crack propagation, unlike the microfibers that only delay cracking creation and are ineffective in restraining it. To cover this problem, it is necessary to add nanofibers using the stiffness of C-S-H gel at the nano level and inhibit the nano cracks propagation. Carbon nanotube (CNTs) is one of the common nanomaterials used as fiber reinforcements to create multifunctional composites with new different characteristics due to their unique mechanical, electrical, and thermal properties [22,23]. It was found that CNTs have proven to be useful in withstanding crack propagation where they work at the micro and nano level in the nano scale [24,25]. They are used as fillers for pores and gaps, resulting in denser reinforcement, in addition to having a great bridging effect that helps in inhibiting the crack propagation as well as delaying the crack formation [26]. The connecting influence between CNTs and cementitious matrix stimulates in increasing transfer of load and stress carrying capacity of material [20,22,23,27,28]. In the past work, many types of research were conducted to determine the relationships of the bond strength between normal concrete and steel rebars, for different effective parameters at ambient and high temperatures [29-31]. It was observed that CNT surfaces would chemically interact with hydration products of concrete and consequently increase the bond strength between CNT and matrix [26]. However, there are limited studies that investigate the bond strength of steel rebar before and after exposure to the corrosion environment of matrix incorporated with CNT. It was observed that the cementitious composites reinforcing by CNTs exhibit lower shrinkage than the control cement paste resulting in lowering autogenous strains [32]. CNTs were then utilized as discrete fibers in increasing the distribution of the stresses and controlling the crack growth within the matrix.

Therefore, NC showed high pozzolanic reactivity and turns the concrete to be denser and well compacted, and CNT has ultra-high-strength and stiffness with extremely high aspect ratios and surface area. Using nanoparticles of NC will improve the bond between CNT and hydrated products surrounding the transition zone. It was reported from the literature that the optimum sonicated nano-clay replacement was 5% by cement weight [5]. However, to the best of our knowledge, the effect of incorporating hybrid NC and CNT on the mechanical strength, microstructure, and durability properties of concrete has not yet been reported. This study aims to investigate the engineering and durability properties of concrete incorporated with hybrid nanomaterials. So this study investigates the influence of incorporation of different percentages of CNTs on nano-clay-based concrete with (5%) constant replacement level by cement weight on concrete when subjected to a corrosive environment. Specifically, the main objective is to determine the porosity, chloride penetration, and corrosion resistance of concrete related to CNTs dosages. To investigate the influence of carbon nanotubes in the fresh properties, the slump test and the air content test were carried out. Besides that, the mechanical properties were implemented by carrying out mechanical testing for the compressive, splitting tensile, flexural, and bond strengths. The experimental program of this research was carried out with four batches of each test, three of them including carbon nanotubes and others without carbon nanotubes. Ultra sonication was employed to disperse both CNTs and NC in water.

2. Experimental Program

2.1. Material

Ordinary Portland cement used was CEM I (42.5 N) according to ASTM C150 [33]. The used nano-clay (NC) was an off-white powder and with a particle size less than 150 nm. The chemical composition of the used NC is shown in Table 1. Multiwalled carbon nanotubes (MWCNTs) were graphene sheets folded in a cylindrical shape with a length of 10–100 micrometer with an internal diameter from 1.5 to 15 nm and an external diameter of 50 nm. Naturally available clean sand with particles size smaller than 5 mm and a specific gravity of 2.58 and fineness modulus of 2.25 was used as fine aggregate. For the coarse aggregate, clean crushed dolomite of maximum size of 12 mm and a specific gravity of 2.69 was used. Aggregates were mixed between the crushed dolomite and fine sand with a percentage of 65% and 35% by weight of cement, respectively. Naphthalene sulfonate based superplasticizer was used; the physical and the chemical properties have schemed in Table 2.

Table 1. The chemical composition of used nano-clay (NC).

Element	SiO ₂	Fe ₂ O ₃	Al_2O_3	CaO	MgO	TiO ₂	Na ₂ O	L.O.I
Content %	61.24	1.06	20.89	0.16	0.22	1.61	0.71	13.12

Table 2. The physical and chemical characteristics of naphthalene sulfonate.

Appearance	Brown free-flowing liquid
Specific gravity@24 °C	1.190
Air-entrainment	Maximum 1%
Nitrate content (%)	Nil
Chloride content (%)	Nil to BS 5075

2.2. Mixing Procedure and Mixture Constituents

To analyze the efficiency of different percentages of CNTs in concrete reinforcement, four concrete samples with 5% NC by weight of cement were produced with similar composition, differing only in the percentage of CNTs. The cement was replaced with CNT at different percentages of 0.01%, 0.02%, and 0.04% by weight with the mix ID NC-CNT₁, NC-CNT₂, NC-CNT₄, respectively. Reference concrete without CNTs was produced for comparison purposes and has the mix ID (CN). The optimal amount of CNTs was determined considering the results of mechanical characterization of concrete specimens. Appropriate dispersion of CNTs was impressive in crack width and bridging microcracks [34,35]. The mixing water was divided into three equal quantities. The first quantity was mixed with NC particles, then sonicated for 10 min. The second quantity was used as an aqueous solution to disperse the CNTs particles. To break down the bundles between

nanotubes, the degree of cavitation was doubled by using the magnetic stirring of homogenizer for 2 min then the sonication process was carried out for 10 min, with continuous stirring with a glass rod at room temperature as stated in previous work [34]. Finally, the third quantity was mixed with the superplasticizer for 2 min.

The mixing process was carried out by mixing the dry mixture then pouring the aqueous solution of NC, after that adding the aqueous solution of CNTs, and finally the aqueous solution of superplasticizer. Each stage of mixing took 2 min. The mixing proportion (kg per 1 m³) is shown in Table 3.

Mix ID	Cement	NC	CNT	Fine Aggregate	Coarse Aggregate	Water	S.P
NC NC-CNT ₁ NC-CNT ₂	427.5 427.46 427.41	22.5	0.045 0.09	597	1109	192	5.4
NC-CNT ₄	427.32		0.18				

Table 3. The Mixing Proportion of designed mixes (kg) per 1 m³.

2.3. Testing

Compaction and curing of all specimens were executed according to the recommendations of ASTM C31 [36]. At the fresh stage, the consistency of concrete was determined by carrying out the workability test according to ASTM C 143 [37]. The air content of concrete was determined according to ASTM C231 [38]. Cubes with dimensions ($100 \times 100 \times 100 \text{ mm}$) were molded for implementing a compressive strength test after 7 and 28 days of curing according to ASTM C109 [39]. Cylinders with dimensions of 100 mm diameters and 200 mm heights were cast and tested after 28 days of curing for the tensile strength test according to ASTM C496 [40]. Further, prisms with dimensions of $50 \times 50 \times 200 \text{ mm}$ were cast and tested after 28 days of curing strength according to ASTM C496 [40]. Further, prisms with dimensions of $50 \times 50 \times 200 \text{ mm}$ were cast and tested after 28 days of curing strength according to ASTM C496 [40]. Further, prisms with dimensions of $50 \times 50 \times 200 \text{ mm}$ were cast and tested after 28 days of curing for the flexural strength according to ASTM C293 [41]. To evaluate the durability in the hardened stage, specimens with dimensions ($50 \text{ height} \times 100 \text{ diameter mm}^2$) were molded for executing sorptivity test after 28 days of curing according to ASTM C1585 [42]. In addition, cubes with dimensions ($150 \times 150 \times 150 \text{ mm}^3$) were cast and tested after 28 days of curing for the water permeability according to CRD-C 163-92 [43].

The chloride penetration resistance was determined according to ASTM C1202 [44]. Cylinders with dimensions $(150 \times 300 \text{ mm}^2)$ were molded for testing chloride penetration resistance for the concrete specimens. Finally, cubes with dimensions $(150 \times 150 \times 150 \text{ with } \emptyset 16$ steel reinforcement) were cast to evaluate the corrosion resistance according to ASTM C876 [45]. Additionally, the bond strength test was carried out on both the corroded and non-corroded re-bars according to RILEM 7-II- 128 [46].

3. Test Results and Discussion

3.1. Air Content

Figure 1 showed the influence of the hybrid nanomaterials on the air content of concrete at the fresh stage. Generally, the air content increased slightly with all replacement levels of carbon nanotubes as compared to the control mix. Air content values were 2, 2.6, 2.4, and 2.1 in the mixes NC, NC-CNT₁, NC-CNT₂, and NC-CNT₄, respectively. The maximum value of the air content test was achieved with a replacement level of 0.01% CNT. This maximum value can be attributed to the small quantities of CNTs particles. The CNTs which have been well dispersed have shown nucleation effect and hence tend to precipitate the particles of nano clay and C-S-H gel on their surfaces. The great specific surface area and the great surface energies of CNTs would significantly enhance sucking the under pressure water inside the nanotubes during the test, thus leading to the increment in the air content. The increment in the air content decreased to 20% and 5% with replacement levels 0.02% and 0.04% of CNT, respectively. This can be attributed to the higher concentration of agglomerated nanotubes bundles. These high concentrations of agglomerated nanotubes bundles would obviously reduce the ability of the CNT in sucking the under pressure water and therefore would decrease the air content value. These air voids, which are considered pores, lead to a decrease in strength as their percent increase [47].



Figure 1. Influence of the hybrid mix on the air content.

3.2. Workability

Figure 2 shows the effect of adding hybrid nanomaterial NC and CNT on the workability of concrete. Generally, the workability was slightly increased in the NC-CNT1 mix and then began to decrease with the increasing addition of carbon nanotubes over (0.01%). The values of consistency were 21.5, 23, 17, 15.5 cm in the mixes NC, NC-CNT₁, NC-CNT₂, and NC-CNT₄, respectively. The workability increased to be 3 cm with adding 0.01% CNT as a replacement of cement weight as compared to the control concrete (21.5 cm). After that, it began to decrease with adding CNT, where the lowest reading reached 155 mm with the cement substitution by 0.04% CNT.



Figure 2. Influence of the hybrid mix on the consistency of concrete.

Consistency of concrete is considered a key boundary to determine the way of transport and status of its fresh properties. From the schemed graph, it is noticed that the workability of concrete slightly increased with adding 0.01% CNT as a cement replacement, which can be attributed to the small amount of CNT that was well dispersed [23,48,49]. Additionally, it was found that CNT contains carboxymethyl cellulose, which is utilized in its manufacturing technology. Carboxymethyl cellulose behaves in an aqueous solution as a thickener and leads to an increase in the dynamic viscosity with high dosages of CNT higher than 0.02% [50]. Another reason is that the high levels of graphene decrease the free available water, thus causes an increment in the frictional resistance between CNT and cementitious matrix leading to higher viscosities [51]. However, the process takes place the opposite way and causes a decrement in the dynamic viscosity at low CNT dosages up to 0.02%. Because the slump is inversely proportional to the viscosity, so it was increased with the decrement in the viscosity and vice versa.

When the used ratio exceeded 0.01% CNT, the workability began to decrease, which may be attributed to the higher dosages of agglomerated CNT particles, thereby exhibiting higher viscosity [51–53]. In addition, with the increase in the amount of CNT, the deformity of the cement matrixes turned hard due to the extrinsic forces [51]. Furthermore, the high surface area and high aspect ratio of CNT caused a higher potential to absorb and require more bulk of water to wet the surface [23,51–53]. Additionally, CNT has an additional influence in locking up extra air content in the mix, all of them causing a reduction of workability [23]. As a final result, the more addition in the CNT content caused a decrement in the initial setting time and promoted the rate of hydration process due to the nucleation effect with reinforcing and setting properties of the cementitious matrix [54].

3.3. Compressive Strength

Figures 3 and 4 show the hybrid effect of adding NC and CNT on the compressive strength of concrete after 7 and 28 days of curing, respectively. Generally, the compressive strength improved after 7 and 28 days of curing with adding CNT as a cement substitution. It was observed that the peak of the compressive strength after 7 days reached 38.7 MPa by adding 0.01% CNT with a gain of 13.8% as compared to the control sample 34 MPa, while the peak after 28 days reached 61.36 MPa with adding 0.04% CNT with gains of about 26.4% as compared to the control concrete.



Figure 3. Compressive strength for the hybrid mix after 7 days.



Figure 4. Compressive strength for the hybrid mix after 28 days.

The improvement in compressive strength may be due to NC showing high pozzolanic reactivity and turning the concrete to be denser and well compacted, and CNT has ultrahigh-strength and stiffness with extremely high aspect ratios and surface area. Additionally, this improvement may be attributed to the presence of CNT, which increased the amount of stiffened C-S-H gel in the nanoscale and created a stronger material. Due to the filling effect of the CNT in the nanoscale, the crack resistance of specimens incorporated with CNT had been improved throughout loading. The larger surface area of CNT helped in improving the stress carrying capacity of the cementitious matrix, as well as enhancing the concentration of stress in the aggregate interface zone. The bond cracks during loading have significantly weakened joints in the heterogeneous cementitious matrix. Debonding and fiber-bridging between CNTs and the C-S-H gel have significantly improved the bonding and the interfacial shear strength of the interfacial transition zone. The presence of CNT retarded the initiation of nano cracks, which in turn enhanced the nano-mechanical characteristics. Moreover, the harmonization between the hydrated products and CNT was very good, which improved the mechanical properties of the nanoscale. The particle size of OPC is normally ranged between 7 and 200 micrometers and the majority of the hydrated products consist of C-S-H gel particles that are considered nanomaterials. Furthermore, the CNT behaves as nucleating agents for calcium silicate hydrates CSH that stimulates and accelerates the cement hydration process and improves the mechanical properties. Besides that, the filling effect of CNT leads to a denser microstructure [55].

After 28 days, the gain was 12.8% in the CNT_1 mix then decreased to 2.9% in the CNT_2 mix. At the age of 7 days, the gain was 13.8% in the CNT_1 mix then decreased to 6% in the CNT_2 mix. This can be attributed to the dominance of CNT bundles and re-agglomeration particles that hindered the pozzolanic activity of NC and prevented the hydration reaction of cement to complete at ages greater than 24 h of curing. Therefore, a reduction in the mechanical properties at later ages is observed [48]. In the CNT_4 mix, an increase in compressive strength results is reported. This increase can be due to the agglomeration of a partial amount of nanotubes while the rest amount worked as fiber reinforcement.

It was observed that the addition of CNT does not appear to have a dramatic effect on the increase in strength. This may be due to the presence of functionalized CNTs causes the formation of large amounts of ettringite, disturbing C-S-H packing on hydration. This leads to the presence of void, preventing the reinforced pastes from achieving their full mechanical performance potential [34].

3.4. Tensile Strength

In general, the incorporation of CNTs was effective in increasing the tensile strength of concrete as shown in Figure 5. This significantly complies with the literature [32].



Figure 5. Tensile strength for the hybrid mix after 28 days.

The improvement in the tensile characteristics and the strain capacity limit can be attributed to the effectiveness of discrete micro- to nano-CNT fibers as a means to control crack growth in cementitious materials. The use of discrete fibers results in a more uniform distribution of stress within the matrix. These nanofibers systems have led to significant improvement in the mechanical properties of cement-based materials [11]. In addition, the distribution of the CNT in the hydrated samples can provide additional bridging in the cracked zone. The incorporation of CNT fibers at the nanoscale will allow the control of the matrix cracks at the nanoscale level and essentially create a new generation of a "crack-free material" [11].

The strength gain was decreased to 2.4% when adding 0.04% CNT. This can be explained by the higher concentration of the CNT particles with poor dispersion, which resulted in the forming of agglomerated bundles, which leads to an increasing in the air voids in the matrix microstructure and caused strength weakness.

3.5. Flexural Strength

Figure 6 shows the influence of the hybrid nanomaterials NC and CNT on the flexural strength of concrete after 28 days. Generally, the flexural strength increased with the addition of nanotubes after 28 days. The peak of flexural strength reached 12 MPa with adding 0.01% and 0.02% CNT as a cement substitution with a gain of about 15.5% as compared to the control sample 10.39 MPa.

The improvement in the flexural strength can be attributed to the carbon nanotubes work at the micro and macro level. So, CNTs are nanoscale particles and can be used as efficaciously fillers for voids and pores leading to generate more effective reinforcement. CNTs behave as reinforcement and they have an efficient effect in restricting crack promulgation in concrete and improving the flexural strength. Furthermore, the remarkable interconnectedness of CNT particles helped in improving the transfer properties of load under stress thus resulting in an enhancement in the strength [56]. The equalization between the size of C-S-H gel and nanotubes with high specific surface area promotes the nucleation effect of CNT. Additionally, it helps them to behave as seeding sites for hydration of cement and accelerates the hydration and strength enhancement. That exhibits an improvement in the load transfer by an increment in the flexure strength [22,57].



Figure 6. Flexural strength for the hybrid mix after 28 days.

The gain decreased to 4% with cement replacement by 0.04% CNT, which can be attributed to the poor dispersion of CNT particles that leads to generating bundles and creating agglomerations. This in turn hindered the pozzolanic reactivity of NC and inhibited the hydration reaction after passing 24 h of curing of cementitious paste [28].

3.6. Sorptivity

Figure 7 represents the influence of the hybrid materials NC and CNT on the sorptivity values of concrete specimens after 28 days of curing. Generally, the incorporation of CNT would slightly increase the sorptivity results. This can be attributed to the full saturation of fine pores of the concrete matrix and therefore the water begins to be sucked inside nanotubes. This would cause particle packing for the concrete matrix. The main objective of applying particle packing is to achieve superior engineering properties, which can be obtained by incorporating the appropriate sizes and percentages of fine particles to pack the larger voids [58,59]. The maximum sorptivity result was achieved in the NC-CNT₁ mix. This complies with the results obtained in the air content test, in which the maximum air content was achieved in the mix with 0.01% CNT.



Figure 7. Influence of the hybrid mix on sorptivity.

3.7. Water Penetration Test

All concrete mixes incorporated CNTs were impermeable due to the presence of NC, so the water penetration depth is used to evaluate the permeability of concrete. Figure 8

shows the influence of the hybrid materials NC and CNT on the water penetration of concrete after 28 days of curing. The highest value of water depth reached was 3 cm by adding 0.01%CNT and the lowest value was 1.5 cm with 0.04% CNT as compared to the control sample 1.2 cm.



Figure 8. Influence of the hybrid mix on the water penetration of concrete.

Therefore, according to the literature, despite the enhancement in pore size refinement, the incorporation of CNTs is not predicted to decrease the total pore volume of the mix, because the percentage of macropores mainly stays the same [22,60,61]. Additionally, the bridging effect may contribute to reducing the total connectivity of the mix, but it does not remarkably change the matrix total porosity. This may demonstrate the reduction of water penetration. The same trend can be achieved in the water penetration tests as that obtained previously in air content and sorptivity. Its peak was achieved with a small amount of CNT (0.01%) and began to decrease with the higher concentration of 0.02% CNT and 0.04% CNT due to the same previous reasons.

3.8. Chloride Penetration Test

All results are classified as very low according to the table of charge passed (coulombs) as an indicator of chloride ion penetration as mentioned in ASTM C879-99. The chloride penetration was 440, 802, 688, and 480 coulombs in the mixes NC, NC-CNT₁, NC-CNT₂, and NC-CNT₄, respectively. The peak of chloride penetration was 802 coulombs with CNT₁ mix and the lowest value was 480 coulombs with CNT₄ mix, as compared to the control sample (440 coulombs) as shown in Figure 9.



Figure 9. Influence of the hybrid mix on the chloride penetration of concrete.

The same trend can be achieved in the chloride penetration test as that obtained previously in air content, sorptivity, and water penetration tests. The higher peak of sucking chloride ions was achieved with the small amount of 0.01% CNT and began to decrease with the higher concentration of 0.02% CNT and 0.04% CNT due to the same previous reasons.

3.9. Corrosion Resistance

Figure 10 showed the influence of the hybrid materials NC and CNT on the corrosion rate of concrete after 28 days of curing after passing one month from the beginning of the test. Generally, the nanotubes improved the microstructure and reduced the rate of corrosion as compared to the control sample. The critical times with considering concrete deterioration reached 23.64, 24.47, and 10.34 years in the mixes NC-CNT₁, NC-CNT₂, and NC-CNT₄, respectively rather than 14.34 years for the control mix according to the corrosion rate classification in RelimTC154 EMC* and ASTM C876-99.



Figure 10. Influence of the hybrid mix on the corrosion rate after 1 month.

The bond strength of 16 mm rebar before and after exposure to the corrosion environment is shown in Figure 11. The reduction in the bond strength as compared to the normal case was 9.4%, 2%, 2%, and 25% in the mixes NC, NC-CNT₁, NC-CNT₂, and NC-CNT₄, respectively.



Figure 11. Influence of the hybrid mix on the bond strength before and after corrosion.

The reduction in the corrosion rate due to adding CNTs as compared to the control concrete can be attributed directly to the CNTs particles that promote and accelerate the cement hydration process. CNTs can act as nucleating agents for calcium silicate hydrates C-S-H [55]. Moreover, the carbon nanotubes increase the amount of stiffness of C-S-H gel resulting in stronger material [27]. Hence, nanomaterials having high specific surface area, acceleration in the hydration process, and strength enhancement have taken place. The nanomaterials have shown a seeding effect in the hydration of cement. Besides this, the size of the nanomaterials promotes the packing effect of the matrix, leading to a denser microstructure [57]. The hydration products include amorphous crystals and crystal water in the size of nanometer-scale to micrometer-scale. The mechanical properties of these products on the macroscale are affected by micro and nanoscale properties. The compatibility between CNTs and the cement hydration products was very good, and that the microstructure of the hydration products improved at the nanoscale. The small size of CNTs helps in reducing the number of fine pores, which leads to the reduction of the capillary stresses, resulting in lower autogenous strains. Hence, CNT reinforced matrix would reduce the length and width of the crack in the concrete and is expected to produce significantly stronger and tougher composites than traditional reinforcing materials [24]. The corrosion rate increased to (5.78×10^{-3}) with the incorporation of 0.04% CNT. This can be attributed to the presence of NC in the cementitious pastes that might prevent the agglomeration of CNT. This can be done through the pozzolanic reaction of NC, which generates extra C-S-H gel that warps CNT in the nanoscale and restrains its agglomeration. As the increase in CNT percentages would suffer from agglomeration phenomena, the CNT is considered to be an electrically conductive material. Therefore, it implies a progressive decrease in the concrete electrical resistivity. This fact contributes to the development of the corrosion cell, which may explain the increase of the I_{corr} values. On the other hand, the galvanic couple between the steel and the conductive carbon material should be taken into account. The union of two different conductive materials with different nobility implies that the less noble element tends to develop higher corrosion rates than the same element without such electrical contact. On the other hand, the material with higher nobility develops lower corrosion rates. The former argument is consistent because the electrons of the less noble material steel will cause cathodic protection on the other one CNT. For this reason, a higher content of CNT implies higher levels of the I_{corr} values [18].

The bond strength decreased by 6% and 28.77% with the cement substitution 0.02% CNT and 0.04% CNT, respectively, as compared to the CNT_1 mix. This can be attributed to a predominance of a re-agglomeration process of CNT that inhibited the pozzolanic activity of NC and hindered the hydration reaction of cement at ages greater than 24 h of curing [28]. In addition to the higher concentration of the CNT, particles got poor dispersion. That resulted in forming bundles and created agglomerations, moreover increasing the air voids in the microstructure.

3.10. Scanning Electron Microscope (SEM)

SEM analysis was carried out to access the different percentages and dispersion quality of CNTs and their interaction with the concrete matrix. From Figures 12–15, the SEM micrographs showed microstructure due to the presence of the hybrid nanomaterials as per the replacement ratio of CNT. Generally, the SEM images reflect the cement matrix and there is no appearance for aggregate in all the images.



Figure 12. SEM micrograph of the NC mix.



Figure 13. SEM micrograph of NC-CNT₁ mix.



Figure 14. SEM micrograph of NC-CNT₂ mix.



Figure 15. SEM micrograph of NC-CNT₄ mix.

The SEM images revealed the variations in the morphology and microstructure before and after incorporating the CNT with the cementitious matrix. It was clear to observe the reason for the achieved modification in the mechanical properties of CNT systems as compared to the control sample.

Formation of extra C-S-H gel, low void ratio, and a small amount of agglomerated NC can be observed in the micrographs of the control sample as shown in Figure 12A,B. It was concluded that the nano clay was well dispersed and possessed a highly pozzolanic reaction. The efficiency of NC in acting as sub-centroplasm and forming a conglomeration of C-S-H gel was significantly observed. These resulted in a good filling effect leading to a compacted and denser matrix.

The scanning images showed the formation of the C-S-H gel, bridging effect of CNT, and low voids in 0.01% CNTs mix as shown in Figure 13A,B. Therefore, the CNTs act as nucleating agents for C-S-H gel. On the other hand, the well-dispersed amount of CNTs could arrest and bridge the cracks which increases the particle packing effect leading to the reduction in the weakest links and hence creating a denser microstructure.

The micrographs of the 0.02% CNTs mix showed small quantities of dispersed CNTs and some agglomerated CNTs and NC as shown in Figure 14A,B. An appearance of obvious voids could also be observed. This was due to the higher concentration of agglomerated nanotubes bundles, which in turn led to the reduction in the mechanical properties. The SEM images of 0.04% CNTs mix are not different from the scanning images of 0.02% CNTs mix. It was observed in Figure 15A,B an appearance of cluster conglomeration of CNTs and NC with widely obvious voids. This observation is due to the agglomeration of some of the nanotube particles while the other particles worked as fiber reinforcement, leading to an increment in the compressive strength.

4. Conclusions

The test results are concluded in the following points:

- 1. In the fresh stage, adding CNT% in the cementitious composites increased the air content of concrete as compared to the control mix. The consistency of concrete slightly increased with the small amounts of carbon nanotubes, while the addition of more CNT caused a decrement in the slump of concrete.
- 2. The maximum peak of compressive strength was 26.4% with 0.04% CNT as compared to the control mix. The maximum peak of tensile strength was 40.4% with 0.02% CNT when compared to the control mix. The maximum peak of flexural strength was 15.5% with both 0.01% and 0.02% CNT when compared to the control mix. The maximum bond strength as subjected to the corrosive environment enhanced with the cement replacement 0.01% CNT as compared to the control concrete.

- 4. The mixtures incorporating CNT% showed a slight increment in sorptivity and penetration depth as compared to the control paste with the same increment trend in chloride penetration.
- 5. From the SEM images, it was concluded that the major effects of CNTs are (1) filling effect, (2) bridging effect, and (3) nucleation as sub-centroplasm for C-S-H gel. These findings comply with the results reported from the mechanical strength and durability tests.
- 6. Hybrid nanoparticles improve the corrosion resistance and have proven useful resistance of crack propagation within the concrete matrix. The engineering properties were significantly improved by using hybrid nanoparticles where the high pozzolanic effect of NC led to improve the mechanical strength, as long as the nanotubes were used to reinforce concrete and, hence, enhanced the durability properties. These results agreed with the measured tests.

Author Contributions: Conceptualization, M.S.E.-F. and M.K.; methodology, M.S.E.-F. and M.K.; validation, Y.R.A. and A.A.A.; formal analysis, H.A.G.; writing original draft preparation, H.A.G.; writing review and editing, M.S.E.-F. and M.K.; visualization, M.S.E.-F.; supervision, M.K.; funding acquisition, Y.R.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Researchers Supporting Project number (RSP-2020/271), King Saud University, Riyadh, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors extend their appreciation to Researchers Supporting Project number (RSP-2020/271), King Saud University, Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

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