Effect of Multi-Walled Carbon Nanotubes on Mechanical Properties of Concrete

Musab Aied Qissab  
Department of Civil Engineering  
Al-Nahrain University, Iraq  
E-mail: musabaq79@gmail.com

Shaymaa Tareq Abbas  
Department of Civil Engineering  
Al-Nahrain University, Iraq  
E-mail: shaimaa.alnaqeeb@yahoo.com

Abstract

The main goal of this paper is to study the effect of different concentrations of long multi-walled carbon nanotubes (MWCNTs) and short MWCNTs on the mechanical properties of concrete (compressive strength, splitting tensile strength, flexural strength and static modulus of elasticity). Ultrasonic pulse velocity test was also used to evaluate the porosity of concrete nanocomposite. 81 specimens with MWCNTs of (0.03%, 0.045%, and 0.06%) by weight of dry cement were tested after 28 days of curing. Dispersion of MWCNTs was achieved by using Ultrasonic Liquid Processors with surfactant. Scanning electron microscopy SEM images for micro-crack bridging was conducted to examine the bonding between MWCNTs and the cement paste. Test results showed that the addition of very low concentrations of MWCNTs led to a reduction in the porosity of concrete composite and significant increase in the amount of high stiffness C-S-H gel. Specimens reinforced with (0.03% short CNT, 0.03% and 0.045% long CNT) showed an increase in density about (1.63%, 0.82%) respectively. In general reinforcing concrete with MWCNTs led to enhance the mechanical properties of concrete nanocomposites compared to the reference samples.

Keywords: Multi-Walled Carbon Nanotubes (MWCNTs), SEM images

1-Introduction

The 21st century considered the century of Nanotechnology which played a central role in producing innovative concrete materials. Concrete is the most used human-made material extensively applied in all of construction projects. The popularity of the material is due to its relatively low cost, high compressive strength, and relatively simple construction technology. Carbon nanotubes (CNTs) attract the researchers since their discovery, because of their higher strength and relatively low weight. These nanotubes are useful for any application where hardness and flexibility are necessary. Further, nanotubes are also stable under extreme chemical environments, high temperatures and moisture as well. It was found that carbon nanotubes can be used to create a new material which exhibits enhanced young’s modulus, tensile strength and improved early a strain capacity.

CNTs have potential for being used as reinforcement materials for concrete, but there is still a serious need for more research studies to complete understand the structural behavior of CNTs as reinforcing materials in concrete. Use of CNTs in concrete would lead to considerable reduction in the dimensions of the structural members which could result in much less consumption of cement. Further, carbon nanotubes can also be used to make nanocomposite steel.

In 1991, SumioIijima [1], published the first article that describes the formation of helical micro tubes made of pure carbon atoms linked together by carbon-carbon (C-C) bonds. These tubes are attracted to each other’s by very strong forces called (Van der Waals), CNTs can be imagined as a graphene sheet rolled in a cylindrical (tube) shape. These rolled tubes can be formed as a single tube with one cylinder, called single-walled carbon nanotubes SWCNTs, or may be made from multiple layers, called multi-walled carbon nanotubes MWCNTs, The diameter of CNTs is (100) thousand times smaller than the diameter of a human hair, as mentioned by Toma, in 2004 [2]. While their lengths usually reach the micrometer range, although centimeters-long. So they have very large aspect ratios (length to diameter ratio). MWCNTs have from tens to hundreds of walls, with typical adjacent walls separations of (0.34) nm as reported by Popov et al, in 2004 [3]. MWCNTs have a tensile strength of 63 GPa (about (100) times stronger than steel) with an ultimate strain capacity of more than (12%) (about (60) times higher ductility than steel) and a Young’s modulus of about (950) GPa[4]. Also CNTs have a very low mass density about (1.3) to (1.4) g/cm3 that varies based on their purity, (about (1/6) of the density of mild steel) as mentioned by Collins et al. in 2000 [5]. MWCNTs are very flexible materials that do not suffer damages in their structure when bend or subject to high pressures, as reported by Wong et al. in 1997 [6]. The average flexural strength was reported between (14.2) ± (8.0) GPa.
Dispersion of CNTs is one of the major factors that strongly influence the properties of nanocomposites. Because these nanomaterials have intense tendency to agglomerate due to attractive forces (Van der Waals) between the tubes [7]. Many methods are used in dispersion of CNTs, but an acceptable dispersion of the CNTs could achieve by using an ultrasonic processor with surfactants in an aqueous solution with a specific amount of energy and sonication time [8]. Many surfactants are successfully used in order to disperse carbon nanomaterials in cementitious matrices. The most surfactant used are Sodium dodecyl benzene sulphonate (SDBS), Triton X-100 (TX10), sodium deoxycholate (NaDC), Gum Arabic (GA), and cetyltrimethyl ammonium bromide (CTAB). These surfactants have not the ability to disperse nanomaterials in water, but they used to wet the nanomaterials with water and improve the dispersion stability [7].

The compatibility between the surfactant which is used to disperse CNTs within cement paste is very important issue. In 2005 Trettin et al. [9], reported in an experiment, "that many of the surfactants that can effectively disperse CNTs in liquids are incompatible with cement hydration; they could delay or even stop the hydration and the hardening process of the cement paste".

One of the most successful surfactants that is compatible with cement without affecting the hydration process was proposed by Yazdanbakhsh et al. in 2010 [10]. In this study, good dispersion of CNTs within the mixing water of cement paste was provided by using an ultrasonic mixer with a commercial superplasticizer, ADVA Cast 575 (polycarboxylate-based water-reducing admixture).

The first authors who highlighted the main advantages of using CNTs within cement paste compared to traditional fibers were Makar et al. in 2003 [11]. In this study the production of CNTs/cement composites was done. Although no mechanical test results were achieved, it was mentioned that CNTs (because of their high strength) would be responsible for a better mechanical stresses distribution by improving and increasing the contact area between the tubes and the matrix.

Because of the difficulty in dispersion of CNTs within cement paste, few researches have been done on the use of CNTs within cementitious materials especially with concrete.

A comparison between long and short MWCNTs as reinforcing materials within cement paste was reported by Konsta et al. in 2010[12]. Effective dispersion of (0.048 wt. %) long MWCNTs and (0.08 wt. %) short MWCNTs with water/cement ratio of (0.5) was achieved by applying ultrasonic energy and with the use of a surfactant. The results are shown that MWCNTs increase the amount of high stiffness C–S–H and decrease the porosity. An increase in flexural strength about (25%) and in Young modulus about 45% was achieved with nanocomposite.

The effect of different types and different dosages of MWCNTs in cement mortar was studied by Manzur et al. in 2010 [13]. Uniform dispersion of CNTs was achieved by a sonication technique. It was found that addition of 0.5 % wt. of MWCNTs result to an increase in the mean strength compared with the control sample; the highest mean compressive strength was provided by addition of 0.3 % wt. of MWCNT. Higher compressive strength was obtained from smaller-sized MWCNTs, because the smaller-size MWCNTs can distributed at a much finer scale and therefore fill the nanopores space more effectively.

Siddik et al. in 2014 [14] studied the influence of addition of (MWCNTs) to concrete. Seventy prism specimens with size of (120 mm width, 20 mm height, and 180 mm length) with different notch lengths were tested with modified Arcan test machine to determine the fracture behavior of concrete. All specimens were prepared by the addition of (0.5%) wt. of MWCNTs, superplasticizer at ratio of (3%) by weight of cement, and with 0.5 w/c ratio. According to the test, it was found that all the specimens having MWCNTs showed an increase in fracture properties of micro concrete. The compressive strength had risen by (7% to 11%), while tension strength showed little increase of (2%), compared to specimens without MWCNTs.

Madhaviet al. in 2013 [15], discussed the strength characteristics and durability of concrete reinforcement with (MWCNTs). Specimens with MWCNTs of concentrations (0.015%, 0.03% and 0.045%) wt. of cement were dispersed by sonication process with 0.25% surfactants (super plasticizers), and with (0.4) water/cement ratio. The specimens were tested for Water Absorption Test, Split Tensile Strength Test, and Compressive Strength Test. Using cylindrical specimens of (150 mm height, and 300 mm diameter), the results indicated that samples with (0.045%) of MWCNT showed a decrease in water absorption by about (17.76%) and increased in compressive strength by (26.69%). Also, the results indicated that splitting tensile strength of MWCNT concrete specimen having (0.045%, 0.03% and 0.015%) was (66.3%, 45.38%, and 30.83%) higher than the conventional concrete specimen.

Gurpreet, in 2014 [16] studied the effect of addition of MWCNTs on strength properties (splitting tensile strength, compressive strength, and young’s modulus) and durability property (permeability) of concrete. In this study, (20%) by
weight of cement was replaced by fly ash and different concentrations of MWCNTs (0.025%, 0.048%, and 0.08%) by weight of (cement + fly ash) were used to prepare five different mixtures. An increase in splitting tensile strength, compressive strength and young’s modulus was observed in mixtures incorporating (0.08%) CNTs and FA (fly ash) in comparison with those containing (20) percent of fly ash.

In order to realize the potential of CNTs in construction industry, further research needs to be carried out on cement mortar and concrete. Up to date most tests have been performed on cement in laboratory scale. This research investigates the behavior of reinforced concrete with MWCNTs.

2. Experimental work

2.1 Material

The test specimens (27) cube specimens of (150mm*150mm*150mm), (27) cylindrical specimens of diameter (150mm and height of 300mm), and (27) prisms of (40mm*40mm*100mm) were tested for (compressive strength, splitting tensile strength, flexural strength and static modulus of elasticity) after 28 days of curing with water.

2.2 Casting

Ordinary Portland cement, river sand passing through (4.75) mm sieves and coarse aggregate of size (10) mm were used. Portable water was used for both mixing and curing. M49 grade concrete was adopted in this study. Water cement ratio is (0.365) and the mix ratio 1: 1.42: 2.14. Sika ViscoCrete-5930 [17] which is a high performance superplasticizer concrete admixture was used as surfactant in this study. The MWCNTs used in this study were provided by Cheap Tubes [18]. This type of MWCNTs was produced by using the catalytic chemical vapor deposition (CCVD) process. The physical properties provided by the manufacturer are given in Table (1).

Table 1: Physical properties of MWCNTs [15]

<table>
<thead>
<tr>
<th>physical properties</th>
<th>long MWCNTs</th>
<th>short MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>OD</td>
<td>&lt;8nm</td>
<td>20-30nm</td>
</tr>
<tr>
<td>Length</td>
<td>10-30um</td>
<td>10-30um</td>
</tr>
<tr>
<td>Purity</td>
<td>&gt;95wt%</td>
<td>&gt;95wt%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;1.5wt%</td>
<td>&lt;1.5wt%</td>
</tr>
<tr>
<td>SSA</td>
<td>&gt;500m²/g</td>
<td>&gt;110m²/g</td>
</tr>
<tr>
<td>EC</td>
<td>&gt;10-³/cm</td>
<td>&gt;10-³/cm</td>
</tr>
</tbody>
</table>

2.3 Preparation of MWCNTs Solution

At first, the required amount of MWCNTs and the required quantities of the mixing water and the surfactant were measured and added together with the MWCNTs into a water- jacketed beaker with a capacity of (2 liters).

Ultrasonic liquid processors Q700 sonicator from QSONICA, LLC. shown in Fig. (1), was used in the dispersion process of MWCNTs solution. The maximum power of Q700 sonicator could reach (700 watt) with a frequency of (20 kHz). Therefore by this high frequency of the ultrasonic waves, a good level of dispersion of the MWCNTs in water can be achieved. During the dispersion process and because of high energy introduced into the solution, temperature of the solution rise up and caused part of the mixture water to evaporate. Therefore, to reduce the temperature of solution below 45°C during and after the dispersion process, the water beaker had surrounded by an ice bath. The ratios of SP, MWCNTs, and the sonication period used in this study are given in Table (2).

Table 2: The ratios of SP and MWCNTs used in this study

<table>
<thead>
<tr>
<th>Type of mixes</th>
<th>Type of CNTs</th>
<th>Superplasticizer % by weight of cement</th>
<th>MWCNTs by weight of cement</th>
<th>Concentration in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference mix</td>
<td>0.65</td>
<td>0.00</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Mix with short CNTs</td>
<td>0.7</td>
<td>0.03%</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Mix with long CNTs</td>
<td>1.3</td>
<td>0.045%</td>
<td>25 (5 on, 1 off)</td>
<td></td>
</tr>
<tr>
<td>Mix with short CNTs</td>
<td>1.3</td>
<td>0.06%</td>
<td>30 (5 on, 1 off)</td>
<td></td>
</tr>
<tr>
<td>Mix with long CNTs</td>
<td>1.3</td>
<td>0.03%</td>
<td>30 (5 on, 1 off)</td>
<td></td>
</tr>
<tr>
<td>Mix with short CNTs</td>
<td>1.3</td>
<td>0.045%</td>
<td>30 (5 on, 1 off)</td>
<td></td>
</tr>
<tr>
<td>Mix with long CNTs</td>
<td>1.3</td>
<td>0.06%</td>
<td>35 (5 on, 1 off)</td>
<td></td>
</tr>
</tbody>
</table>
2.4 Mixing of Carbon Nanotube Solutions with Concrete

To make CNTs/concrete composite, firstly cement, coarse aggregate and fine aggregate were dry mixed. After drying mixing MWCNTs—water mixture solution was added to dry mix and rapid mixing is done to avoid any chance of agglomeration. Then the concrete was poured into greased molds with two layers; each layer was compacted by using a plunger mechanical vibrator. Then they were de-molded after 24 hours, and cured in water for 28 days. After that, the beams and specimens were tested.

3. Results and discussion

3.1 Ultrasonic Pulse Velocity Result

This test was done on (150mm x 150mm x 150 mm) cubes by using an ultrasonic testing machine type (V-Meter MK III). The ultrasonic pulse velocity and the density results are summarized in Table (3). These results show that the velocity of the transverse wave and the density of the mixture were increased with the addition of MWCNTs.

Table 3: Ultrasonic pulse velocity result

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Ultrasonic pulse velocity (m/sec)</th>
<th>Density (kN/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-reference specimens</td>
<td>3115.88</td>
<td>23.24</td>
</tr>
<tr>
<td>B2- 0.03% short</td>
<td>3179.8</td>
<td>23.62</td>
</tr>
<tr>
<td>B3- 0.045% short</td>
<td>3225.5</td>
<td>23.35</td>
</tr>
<tr>
<td>B4- 0.06% short</td>
<td>3252</td>
<td>23.31</td>
</tr>
<tr>
<td>B5- 0.03% long</td>
<td>3149.7</td>
<td>23.43</td>
</tr>
<tr>
<td>B6- 0.045% long</td>
<td>3179.11</td>
<td>23.43</td>
</tr>
<tr>
<td>B7- 0.06% long</td>
<td>3157.66</td>
<td>23.30</td>
</tr>
</tbody>
</table>

3.2 Compressive Strength Results

The test was conducted according to BS 1881: part 116:1983 [19] specimens on cubes of size (150 x150 x 150 mm) after 28 days of curing. According to the test results, it is clear that the compressive strength for all specimens increased with the addition of MWCNTs. The reason of this increment because MWCNTs occupied the nanostructure of cement paste and increase the concrete cracking resistance during the period of loading. Compressive strength result is presented in Table (4) and Fig. (4).

3.3 Splitting Tensile Strength Results

The splitting tensile strength test was carried out on cylindrical specimens (150 x300 mm) in accordance to the ASTM C496/C496M-04 [20]. The maximum increase in tensile strength was obtained with (B6) with (0.045%) of long MWCNTs. While for (B7) the value of tensile strength less than that for reference mixture. This may be relating to the poor dispersion of MWCNTs within cement paste. The results of splitting tensile strength are presented in Table (4) and Fig. (5).

3.4 Flexural Strength Result

The flexural strength test was carried out on concrete prisms of dimensions (100*100*400 mm) with a span of 300 mm which were casted according to ASTM C-78, 2002 [21] specification. All specimens with MWCNTs showed an increase in their flexural strength compared to the reference specimen. It is observed that the value of flexural strength decreases with the increment of short MWCNTs concentration. While an increase in flexural strength is observed with increase the concentration of long MWCNTs, and the maximum increment in flexural strength obtained by adding (0.03%) short MWCNTs. The results of this test are presented in Table (4) and Fig. (6).
3.5 Static Modulus of Elasticity

The static modulus of elasticity was determined according to ASTM C469-02 [22] specifications by testing a cylinder of dimensions (150* 300mm. The results of this test are given in Table (4) and Fig. (7). The results show that the static modulus of elasticity for all specimens increased with the addition of MWCNTs especially for specimens (B3) and (B5). This increment in modulus of elasticity of nanocomposite because CNTs have a modulus of elasticity equal to (1000) GPa. Accordingly, the addition of these materials to concrete even in very low concentration will enhance its modulus of elasticity and make the concrete stronger.

### Table 5: Results of tests for concrete specimens

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Comp. str.</th>
<th>% increase</th>
<th>Str. tensile</th>
<th>% increase</th>
<th>Flexural str.</th>
<th>% increase</th>
<th>Elasiticity GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>49.8</td>
<td>-</td>
<td>3.33</td>
<td>-</td>
<td>4.03</td>
<td>-</td>
<td>31.2</td>
</tr>
<tr>
<td>B2</td>
<td>54.4</td>
<td>9.1</td>
<td>4.26</td>
<td>28.05</td>
<td>4.81</td>
<td>19.08</td>
<td>33.9</td>
</tr>
<tr>
<td>B3</td>
<td>56.2</td>
<td>12.7</td>
<td>3.89</td>
<td>16.82</td>
<td>4.58</td>
<td>13.37</td>
<td>35.6</td>
</tr>
<tr>
<td>B4</td>
<td>55.3</td>
<td>10.9</td>
<td>3.43</td>
<td>3.15</td>
<td>4.53</td>
<td>12.15</td>
<td>33.1</td>
</tr>
<tr>
<td>B5</td>
<td>55.2</td>
<td>10.7</td>
<td>3.88</td>
<td>16.58</td>
<td>4.15</td>
<td>2.74</td>
<td>36.2</td>
</tr>
<tr>
<td>B6</td>
<td>60</td>
<td>20.3</td>
<td>4.58</td>
<td>37.51</td>
<td>4.54</td>
<td>12.35</td>
<td>32.3</td>
</tr>
<tr>
<td>B7</td>
<td>55</td>
<td>10.3</td>
<td>3.27</td>
<td>-1.65</td>
<td>4.57</td>
<td>13.14</td>
<td>31.8</td>
</tr>
</tbody>
</table>
The images indicate that many of CNTs are bridging the micro-crack of cement paste.

The breakage of MWCNTs implies a good bonding between the cement paste and the CNTs surfaces. Also these images indicate that very high stress applied to these nanomaterials which mean that more CNTs are needed to carry this stress. Fig. (11) for B (7) shows the breakage of MWCNTs in the micro-crack of cement paste.

4. Conclusions

1. The addition of very low concentrations of MWCNTs led to a reduction in the porosity of concrete composite and significant increase in the amount of high stiffness C-S-H gel. Specimens reinforced with (0.03% short CNT, 0.045% long CNT) showed an increase in density about (1.63%, 0.82%) respectively.

2. Specimens reinforced with (0.045% short CNT, 0.045% long CNT) showed an increase in compressive strength about (12.72%, 20.34%) respectively more than the reference specimens.

3. Maximum increase in splitting tensile strength observed with specimens reinforced with (0.03% short CNT, 0.045% long CNT) about (28.056%, 37.52%) respectively more than the reference specimens.

4. Specimens reinforced with (0.03% short CNT, 0.06% long CNT) showed an increase in flexural strength about (19.08%, 13.14%) respectively more than the reference specimens.

5. Maximum increase in static modulus of elasticity observed with specimens reinforced with (0.045% short CNT, 0.03% long CNT) about (14%, 15.98%) respectively more than the reference specimens.

6. The addition of MWCNTs to concrete reduces the workability of the concrete mixture. The decrease in workability increases directly proportional to the ratio of MWCNTs additive.

7. The only method to measure the dispersion of the CNTs within the cement paste composite by using SEM images, these images covered a limited volume of cement paste composite.

8. The mechanical properties of concrete may be improved or adversely affected with the addition of CNTs, depending on the concentration of CNT, the water/cement ratio and the effective dispersion of the CNT in the concrete composite.

5. Acknowledgements

The authors wish to acknowledge the support of National Center for Construction Laboratories and Research and Consulting Engineering Bureau at Baghdad University. And the support of the Civil Engineering Laboratory of Al-Nahrain University. Also the authors wish to acknowledge the support of University of Technology/Department of Production Engineering and Metallurgy which supported the microscopy images.

6. References


تأثير انابيب الكربون النانوية متعددة الجدران على الكونكريت

شيماء طارق عباس
قسم الهندسة المدنية / كلية الهندسة
جامعة النهر
E-mail: shaimaa.alnaqeeb@yahoo.com

MSCUB عاد كصب
قسم الهندسة المدنية / كلية الهندسة
جامعة النهر
E-mail: musabaq79@gmail.com

الخلاصة

الهدف الرئيسي من هذه البحث هو دراسة تأثير تركيز مختلف من انابيب الكربون النانوية متعددة الجدران (الطويلة والقصيرة) على الخواص الميكانيكية للكونكريت مثل (مقاومة الانضغاط، مقاومة الشد، مقاومة الانحناء ومعامل المرونة). تم استخدام الفحص بالموجات فوق صوتية لغرض تقسيم مسامية الكونكريت. تم استخدام نموذج من الكونكريت مضاعف البه تراكيز مختلفه من انابيب الكربون النانوية متعددة الجدران (0.03، 0.045، 0.06) % من وزن السمنت الاجمالي.

تمت عملية تشتيت انابيب الكربون النانوية متعددة الجدران باستخدام جهاز معالج السوائل باستخدام الموجات فوق صوتية نوع Q700 ومساعدة الملون الفائق سيك - 59.5. تم استخدام صور المجهر الإلكتروني SEM لفحص مناطق الصدع الدقيقة وذلك لفحص فحص التلاصق بين انابيب الكربون النانوية متعددة الجدران وعاج السمنت.

أظهرت نتائج الفحوصات أن إضافة تركيز قليل من انابيب الكربون النانوية متعددة الجدران يؤدي إلى نقصان في سوية الكونكريت وزيادة ملحوظة في الكثافة الناتجة من إضافة السمنت. أظهرت نماذج الكونكريت التي تحتوي على (0.03% انابيب كربون قصيرة، 0.03% و 0.045% و 0.06% انابيب كربون طويلة) زيادة ملحوظة في الكثافة بمقدار (1.63% ، 0.12% و 0.06%). بشكل عام أظهرت نماذج الكونكريت المسلحة بانابيب كربون نانوية متعددة الجدران تحسن في الخواص الميكانيكية مقارنة بالنماذج المرجعية.