SEM/AFM studies of cementitious binder modified by MWCNT and nano-sized Fe needles

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ABSTRACT

Several compositions of cement paste samples containing multiwalled carbon nanotubes were produced using a small-size vacuum mixer. The mixes had water-to-binder ratios of 0.25 and 0.3. Sulfate resistant cement has been used. The multiwalled carbon nanotubes were introduced as a water suspension with added surfactant admixtures. The used surfactant acted as plasticizing agents for the cement paste and as dispersant for the multiwalled carbon nanotubes. A set of beams was produced to determine the compressive and flexural strengths. The scanning electron microscope and atomic force microscope studies of fractured and polished samples showed a good dispersion of multiwalled carbon nanotubes in the cement matrix. The studies revealed also sliding of multiwalled carbon nanotubes from the matrix in tension which indicates their weak bond with cement matrix. In addition to multiwalled carbon nanotubes also steel wires covered with ferrite needles were investigated to determine the bond strength between the matrix and the steel wire. These later samples consisted of 15-mm-high cylinders of cement paste with vertically cast-in steel wires. As reference, plain steel wires were cast, too. The bond strength between steel wires covered with nano-sized Fe needles appeared to be lower in comparison with the reference wires. The scanning electron microscope studies of fractured samples indicated on brittle nature of Fe needles resulting in shear-caused breakage of the bond to the matrix.

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1. Introduction

The properties of the cement matrix, especially its microstructure and chemical composition have a major influence on strength and durability of concrete. The brittle nature of the cement matrix and the existence of a weak transition zone in the vicinity of aggregates or reinforcement are among factors that attract significant attention within the researcher community. The introduction of a new generation of so-called nanomaterials, provided a number of new approaches to modify these concrete properties. One of the most difficult but potentially very advantageous is the usage of carbon nanotubes (CNTs) for nanostrengthening of the cement matrix.

CNTs are characterized by their outstanding mechanical properties [1]. Young’s modulus is estimated to vary between 1000–5000 GPa while density is around 2000 kg/m³ [2–4]. The CNTs are characterized by thermal stability up to 2800 °C; thermal conductivity compared to diamond is twice as good, and the electrical conductivity is about 1000 times better than copper. These mechanical and physical properties have built up high expectations regarding the use of carbon nanotubes in various fields such as molecular electronics or advanced materials. All above given values relate to a single nanotube. CNTs obtained during production are packed together by van der Waals attraction forces into crystalline ropes. The ropes, on the other hand, form triangular lattices which tend to aggregate.

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and result in a lack of ability of CNTs powder to disperse in aqueous or organic solutions [5]. A way to overcome this problem is to increase the solubility in water by the addition of "polar impurities" such as OH or COOH end groups. Another approach to improve the solubility is to use polymers. In this case, the steric repulsion among polymer-decorated CNTs stabilizes the CNTs dispersion [5,6]. The results by atomic force microscope (AFM) showed that polymer-single walled carbon nanotubes have a constant diameter along their length suggesting that the polymers were wrapped around the tubes and were not associated with the walls at various locations as random coils. Some research was also done on growing polymer chains directly on CNTs. The common way is to use the so-called "grafting", which involves the attachment of certain radicals to the tips or convex walls of CNTs. The next stage involves polymer growing, using for instance esterification or radical coupling [7].

The second main problem when using CNTs is their weak bonding to the cement matrix. There is very limited knowledge about the actual strength of this bond. Some tests were done for instance by Kowlad [8] who compared the compressive strength of cement paste specimens incorporating COOH functionalized CNTs and pure CNTs. The present study focused primarily on the effect of CNTs on the mechanical properties of the cement paste, and on the effects of surfactants on the distribution of CNTs within the cementitious matrix. The studies were supported by scanning electron microscope (SEM), transmission electron microscope (TEM) and AFM investigations. The results showed a very limited increase of the strength but a strong influence of the CNTs on the workability of the paste.

A secondary objective was to study the effect of the nanosized Fe needles, grown on the steel wires, on the steel-binder matrix bond strength.

2. Materials and Methods

The first part of this study included the preparation of carbon nanotube dispersion in water, their incorporation into the cement paste and the determination of the 28-days compressive and flexural strength. The multi-walled carbon nanotubes (MWCNTs) used in this research were produced by a chemical vapor deposition (CVD) method [9,10]. The CNTs had a maximum length of 10 µm and diameters of around 10 nm. The CNTs were delivered in powder-form as seen in Fig. 1. The dispersion of pure MWCNTs was obtained by using entropic interactions of polyacrylic acid polymers obtained from a commercially available superplasticizer. The process included dispersion of MWCNT bundles in water using two minutes of sonification at 50 Hz. After the CNTs were dispersed, the polymers were introduced into the suspension and sonification continued for another 30 seconds. Three mixtures containing 0.023-0.14% of CNTs and 2.1% of polyacrylic acid polymer were produced (Table 1).

Sulfate resistant (SR) cement type CEM I 42.5 N (SR) produced by Finnsementti was used for all mixes. The cement consisted of 68% C3S, 13% C3A, 1% C3A and 13% C2AF. The specific surface area was 360 m²/kg and the density 3100 kg/m³. This type of cement was chosen due to its known limited interaction with the superplasticizers.

In order to determine the stability of the dispersion of the CNTs during the mixing process of the cement paste and to study the effect of CNTs on the compressive and the flexural strength, the non-standardized test beams having dimensions of 10×10×60 mm³ were produced. The small size of the specimens was dictated by a very limited amount of the available CNTs. Teflon moulds made in-house were used to avoid contamination of the sample surfaces by released oil. To decrease scatter in the results due to inhomogeneous microstructure (e.g. due to air voids) a small volume vacuum mixer was used. No vibration was applied to any of the test specimens. Mixtures incorporating pure CNTs had a water to cement ratio of 0.25 or 0.3. Higher water to cement ratio was avoided due to increasing inhomogeneity of the hydrated binder matrix. The amount of CNTs, calculated according to cement weight, varied from 0.007 to 0.042% in the case of a water to cement ratio of 0.3 (see Table 2). Cement pastes having water to cement ratio of 0.25 contained from 0.006 to 0.035% of CNTs. Three dosages of polymers were used, the reference paste contained 0.52%, mixes having water to binder ratio of 0.3 contained

![Fig. 1 – Low magnification SEM image of carbon nanotube powder.](image-url)

Table 1 – Mixtures of water, pure CNTs and polyacrylic acid polymer, [12].

<table>
<thead>
<tr>
<th>Mix</th>
<th>Amount of CNT [weight % of water]</th>
<th>Amount of polymer [weight % of water]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK1</td>
<td>0.023</td>
<td>2.1</td>
</tr>
<tr>
<td>MK2</td>
<td>0.1</td>
<td>2.1</td>
</tr>
<tr>
<td>MK3</td>
<td>0.14</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 2 – Composition of the various mixtures, [12].

<table>
<thead>
<tr>
<th>Test specimen</th>
<th>Water to cement ratio</th>
<th>Amount of CNT [% of the cement weight]</th>
<th>Amount of polymer [% of the cement weight]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.3</td>
<td>0</td>
<td>0.52</td>
</tr>
<tr>
<td>5MK1</td>
<td>0.3</td>
<td>0.007</td>
<td>0.63</td>
</tr>
<tr>
<td>6MK2</td>
<td>0.3</td>
<td>0.03</td>
<td>0.63</td>
</tr>
<tr>
<td>7MK3</td>
<td>0.3</td>
<td>0.042</td>
<td>0.63</td>
</tr>
<tr>
<td>8MK1</td>
<td>0.25</td>
<td>0.006</td>
<td>0.49</td>
</tr>
<tr>
<td>9MK2</td>
<td>0.25</td>
<td>0.024</td>
<td>0.49</td>
</tr>
<tr>
<td>10MK3</td>
<td>0.25</td>
<td>0.035</td>
<td>0.49</td>
</tr>
</tbody>
</table>
0.63% and 0.58% of CNTs were added in the case of water to cement ratio of 0.25. The different dosages of polymers and CNTs according to the cement weight related directly to the amounts present in produced dispersions shown in Table 1.

The flexural and compressive strength of the produced specimens was determined using a regular testing machine with a 50 kN force sensor and equipped with an in-house made specimen holder. The procedure included a bend test followed by compression of the obtained beam-half.

The second part of the study included the determination of the effect of nano-sized Fe needles on the bond between the steel wire and cement matrix. The nano-sized iron needles were grown on steel wires by the CVD method. The needles appeared to have lengths from 2 to 10 µm and diameters of few nanometers to 1 µm. In the next step, the wires were cast into cylinders having 20 mm in diameter and a length of 15 mm. The cement paste had a water to cement ratio of 0.3 and no additions of CNTs or superplasticizer.

3. Results

3.1. Dispersion of Carbon Nanotubes

The application of sonification caused a temporary dispersion of the CNTs powder restricted to the duration of the process. Immediately after stopping the sonification, the re-agglomeration occurred due to attractive van der Waals forces of the CNTs acting on each other [6]. In order to prevent this conglomeration a polyacrylic acid polymer, a polyether type containing carboxylate group superplasticizer, was introduced into the solution during sonification. The mixture obtained was stable for two hours with subsequent progressive sedimentation of the nanotubes at the bottom of the beaker. Tests showed that after evaporation of the water at room temperature from a previously prepared dispersion of CNTs it was sufficient just to re-introduce water and mix it by stirring to obtain dispersion.

Incorporation of the water suspension containing pure CNTs and polyacrylic acid polymers did not cause any remarkable change in the cement paste fluidity. The polymers acted as regular superplasticizers and their effectiveness was not visibly influenced by the presence of the CNTs.

3.2. Compressive and Flexural Strength

The results of compressive and flexural strength tests are shown in Fig. 2. The obtained values revealed that the addition of the multiwalled carbon nanotubes did not enhance the mechanical properties of the studied cement paste specimens. The increase of the compressive and flexural strength observed for specimens 8, 9 and 10 was caused by lower water to binder ratios only (see Table 2).

The SEM investigation of fractured specimens showed well dispersed CNTs which could be found in the microcracks and at fractured surfaces (see Fig. 3).

3.3. Bond Strength Between Cement Matrix and Modified by Nano-sized Fe Needles Steel Wire

The presence of strongly bonded CNTs should improve the bond strength between the cement matrix and the steel wire. The SEM investigation of fractured specimens showed well dispersed CNTs which could be found in the microcracks and at fractured surfaces (see Fig. 3).
As growing CNTs directly on the steel fibers appeared to be challenging and time-consuming, studies of steel wires modified with Fe-needles were performed.

The Fe nano-sized needles produced by the CVD method appeared to have lengths from 2 to 10 µm (Fig. 5). The cross section of the needle had a cone-like shape with a bigger diameter at the bottom and smaller at the tip of the needle. The diameters appeared to vary significantly from a few nanometers up to even 1 µm. The surface of the steel wire was not completely covered by the needles. The needles appeared to be brittle, as shown during SEM examination directly after the growing processes.

The results of the pull-out test are shown in Fig. 6. Average values from three samples are shown. The measured maximum pull out-force decreased by nearly 50% in the case of steel fibers covered by nano-sized Fe needles in comparison with a clean steel wire used as a reference.

4. Discussion

The produced stable CNT/polymer/water dispersions indicate a possible association of the polymers with the surfaces of CNTs. The polymer wrapping, described by O’Connell et al. [5], is less probable due to the larger diameters of the MWCNTs used in the present study. Other forms of bonding such as ionic or covalent bonding could occur. The SEM image of the CNTs after water evaporation showed their embedment into a polymer matrix (Fig. 7).

The tendency of sedimentation of the CNTs after long storage times might indicate insufficient amount of polymer. However, because different ratios of CNTs to polymers were studied (see Table 1), it is also possible that the created repulsive forces between the CNTs were simply too weak to sustain the dispersion over a longer period [6]. Strength and...
range of the repulsive forces depend on the polymer chain length and surface density. Nevertheless, the transmission electron microscope image shown in Fig. 8 revealed that our samples contained well dispersed CNTs. SEM investigation revealed well dispersed CNTs as observed in the fractures samples. The CNTs were visible attached to one side of the fracture and disconnected from the other. These results confirm earlier observations by Makar et al. [11] whose studies revealed a crack bridging function of the CNTs incorporated into a cementitious matrix. His results did not show however, whether the CNTs had any impact on the compressive strength. The present results show that the bonding between the multiwalled carbon nanotubes and the cement matrix is very weak. Under tension, the nanotubes are simply pulled-off the matrix with little resistance. Furthermore, the presence of the surfactant polymers at the CNTs surface did not appear to have any effect on the bond strength. Regarding these results, it seems probable that there was no strong physical or chemical bond between CNTs and polymers. The tensile stresses created during mechanical tests would simply slide the CNTs from the polymers and the cement matrix. These results are in agreement with the previous studies about incorporation of CNT into other matrices and show the need for chemical surface treatment of the CNTs to provide their bonding with the matrix and to enhance the mechanical properties of the composites [8]. The increase of compressive strength recorded by some researchers after addition of untreated CNTs into the cement matrix could be caused by other factors [8]. The main reasons could be for instance an effect of the air content. Also, different amounts of the superplasticizers may have altered the workability and resulted in a more homogenous microstructure.

The results obtained while testing the steel wires modified with Fe-needles did not showed any enhancement of the bond strength with the binder matrix. This can be directly attributed to the brittleness of the needles, which decreased a load transfer to the cement matrix in comparison with the reference specimens. A presumably strong bond between steel wire and Fe needles, at least at the very base of the needle was insufficient to have any positive effect. The shearing stresses developed during the pull-out test rapidly cracked the needles and enabled the free movement of the wire resulting in lower ultimate bond strength.

5. Conclusions

The effects of the incorporation of multi-walled carbon nanotubes into the cement matrix and application of a steel wire covered with nano-Fe needles on the mechanical properties were studied. The carbon nanotubes were introduced into the cement paste as dispersed in water with addition of surfactants. The obtained dispersion was uniform but stable for only two hours followed by progressing sedimentation. The interaction between the CNTs and the polymers produced a dispersion without the need for sonification, even after drying and subsequent addition of water. This property can be utilized to produce polymer matrix-embedded CNTs, readily water-dispersible by simple stirring. Additionally, the polymers will act as a regular superplasticizer when mixed with cement and water.

The results showed no increase of either the compressive or bending strength of the cement paste incorporating CNTs in comparison with pure cement paste having the same water to cement ratio. Even though a crack bridging mechanism of present CNTs was observed in fractured cement paste specimens the bond strength with the cement matrix was very low. The association of polymers with CNTs appeared to only enhance the dispersion ability of the CNTs, but did not influence the bond strength to the matrix. These results confirmed earlier observations that in order to provide a sufficient transfer of load between the cement matrix, or any other matrix, and the CNTs, a functionalization of their surface has to be performed. The functionalization should provide chemical bonding with cement paste.

The second part of the study revealed that it is possible to grow nano-sized Fe needles on a steel surface using the CVD method. The obtained needles grew perpendicular to the substrate surface and had lengths from 2 to 10 µm. The pull-out tests performed on the wires covered by the Fe-needles revealed a 50% drop of the pull-out force in comparison with plain steel wires. The results showed that despite a strong chemical bonding between the needles and the steel wire their
brittleness prevents the transfer of the shear forces. Consequently, the bond strength between steel wire and the cement matrix was lower.

REFERENCES