CEMENT GRAINS WITH SURFACE-SYNTHETIZED CARBON NANOFIBRES: MECHANICAL PROPERTIES AND NANOSTRUCTURE

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Abstract

The carbon nanotubes were synthetized directly on the surface of Portland cement particles. Mixing this new carbon/cement material with ordinary cement creates a modified cementitious substance, where carbon is perfectly dispersed in the volume. In presented work was measured the fracture energy and compressive strength of cement paste/mortar created from this new material. The composites with weight fractions of carbon nanotubes/paste in the ranges 0-0.038 were prepared and mechanically tested. Slight increase in fracture energy and compressive strength was observed even in the low carbon weigh fraction 0.019.

Keywords: Carbon, cement, fracture energy, mortar, nanotubes, paste

1. INTRODUCTION

The main objective of this work is to show the mechanical properties of the cement paste/mortar reinforced with carbon nanofibres/nanotubes (CNT/CNF) directly synthetized on the cement particles. Elimination of the demanding dispersion of CNT in the volume is the main advantage of the synthesis of the CNT/CNF on the cement grains surface. Fig. 1 shows the SEM image of the CHM, the Portland cement particles are completely covered with the CNF.

The fracture energies and compressive strengths of the cement composites build from cement modified by the CNT, the so called cement hybrid material (CHM), were measured. The compressive strength of the cement paste increases with the amount of CHM in the mixture, on the contrary the compressive strength of mortar decreases with the amount of CHM in the mixture. This phenomenon is partially explained by the ITZ behaviour, CHM properties and by fracture mechanics.

High performance cement composites produced in last decade exhibit high compressive strength however they have extremely brittle failure, low tensile capacity and high autogenous

Fig 1. SEM image of the CNF synthetized directly on the cement grains surface. Overtaken from L. Nasibulina et al. [1].
shrinkage [2]. Simultaneously to become more sustainable, the amount of Portland clinker in common cement has been reduced and partially replaced by secondary cementitious materials. The further reduction is possible when the strength of the binder could increase. It seems from other applications of carbon nanotubes/nanofibers [2], that the CNT/CNF reinforcement at the nanoscale presents feasible solution.

2. MATERIALS AND METHODS

2.1 Cement binder, CHM, aggregates

The cement, CEM I 42.5 R originated from Mokrá, the Czech Republic, was used as the source material for all specimens. Specific Blaine surface has the value of 306 m²/kg. The chemical composition is given in the Table 1.

The cement hybrid material (CHM) was synthesized by L. Nasibulina et al. by the chemical vapor deposition method [1]. The Portland sulfate-resistant cement (CEM I 42.5N) was used as the base for CNT/CNF growth, see Table 1 for the chemical composition. In the synthesis, acetylene was utilized as the main carbon source for its low decomposition temperature and affordability; CO and CO₂ presents promoting additives [1]. The CNT/CNF growth runs at temperature about 600°C in fluidized bed reactor see Fig. 2 for the scheme of the reactor [1]. The CNT typically grown on the cement particles are 30 nm in diameter and 3 µm in length [3], the specific surface area of CNT is about 10 – 20 m²/g. CNT exhibit elastic modulus in the range of 180 - 588 GPa and tensile strength from 2 to 6 GPa [3, 4].

Pure silica sand, fraction 0 – 2 mm was utilized in the mortar specimens. Three fractions PG1 (0 – 0.25 mm), PG2 (0.25 – 1 mm) and PG3 (1 – 2 mm) were mixed in the ratio 1:1:1.

2.2 Specimen preparation

Cement grains overgrown by carbon nanotubes were utilized in our experiments. Five cement paste and five mortar sets of specimens were casted. The water/binder ratio was set to 0.35 and the carbon nanotubes/paste ratio varied from 0.0 to 0.038. The CHM was intermixed with pure cement and (in case of

Table 1: Oxide Component Content of CHM Base Cement and Cement originated from Mokrá

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CHM-Base Cement</td>
</tr>
<tr>
<td>CaO</td>
<td>63.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20.2</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.2</td>
</tr>
<tr>
<td>MgO</td>
<td>2.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.5</td>
</tr>
</tbody>
</table>
mortar) with dry silica sand; the water with superplasticizer was added at the end. Table 2 shows the specimens composition. The hand stirring took four minutes, consecutive vibrating and form filling took extra four minutes. The specimens sized 40x40x80 mm were cured in water bath at ambient temperature.

After 28 days of curing were the specimens cutted on diamond saw; in the case of the paste specimens were cutted to nine parts (approx. 13x13x80 mm), in case of mortar to four parts (approx. 19x19x80 mm). According to RILEM standards for mechanical testing [5.] nodies were cutted in the middle of the beams to the 45% of the height. The production of such small sized specimens this way is much more efficient than direct casting into small molds. The casting and vibration of small amount of material is ineffective and the quality of specimens (including surface caverns or material inhomogenity) is significantly worse than the quality reached by cutting from larger bodies.

**Table 2**: Cement paste and mortar composition; weight fractions per one sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>total binder weight</th>
<th>cement hybrid material</th>
<th>w/binder ratio</th>
<th>total weight of water</th>
<th>super plasticizer (63% water)</th>
<th>sand fraction 0 - 2 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste</td>
<td>234 g</td>
<td>0 - 70.2 g</td>
<td>0.35</td>
<td>81.9 g</td>
<td>0.47 g</td>
<td>–</td>
</tr>
<tr>
<td>Mortar</td>
<td>75 g</td>
<td>0 - 22.5 g</td>
<td>0.35</td>
<td>26.25 g</td>
<td>0.38 g</td>
<td>225 g</td>
</tr>
</tbody>
</table>

2.3 Fracture energy determination

The fracture energy, $G_f$, was determined according to the RILEM standard [5.]. See Fig. 3 for the experiment scheme. Three point displacement-controlled bending test was carried out to obtain the load-displacement curve. The work of external force $P$ could be calculated as

$$W_f = \int_0^{u_f} P \, du,$$

\text{Eq. 1,}

where $P$ is the external force, $u$ is the load-point displacement and $u_f$ presents the final displacement at which the load is equal to zero. The average (effective) fracture energy in the ligament, according to the RILEM standard, is defined as

$$G_f = \frac{W_f}{bl}, \quad l = h - a_0,$$

\text{Eq. 2,}

where $l$ represents the length of the ligament, $b$ the thickness of the beam, $h$ the total height of the beam and $a_0$ is the depth of the nodge. The support span $L$ was in case of mortar set to 65 mm and in case of cement paste 50 mm.
3. RESULTS AND DISCUSSION

3.1 Compressive strength

The measurements on the paste samples have shown that replacing 3.5% cement with CHM could increase the compressive strength by 25%, in our case from average 56 MPa to average 70 MPa. However, in the case of mortar samples, the effect of CHM was negative. The mortar samples with 7% replaced cement exhibit a 15% lower compressive strength, in our case decrease from average 62 Mpa to average 53 Mpa. See Fig. 4 for the compressive strengths of mortar and paste samples with different cement/CHM ratio.

3.2 Fracture energy

The fracture energy measurements results are depicted on the Fig. 5. The paste samples exhibit significant increase in the fracture energy even if a small amount of cement is replaced by CHM. Replacing 3.5% of cement causes an increase in the fracture energy of 14%. The mortar samples does not exhibit almost any change in the fracture energy with the amount of CHM in the mixture.
3.3 Hypotheses

Let us introduce several hypotheses partially explaining the behavior of cement paste/mortar with the CHM. The paste samples reinforced with the carbon nanotubes exhibit the expected increase as in the compressive strength as in the fracture energy. The CNT appear as a nano-reinforcement improving the gel properties [6.]. The compressive strength maximum around 3.5% of CHM can be caused by the strong hydrophobicity of the carbon nanotubes, preventing the larger amount of CHM from hydration. The decrease in the compressive strength of the mortar samples could be described by the non-homogenous gel formation. The carbon nanotubes appear as the nucleating sites [7.] for the cement hydration products (CSH gel, calcium hydroxide) and gather the cement paste. The water is pushed to the sand grains, into the interfacial transition zone (ITZ), which is anyway the weakest point in the mortar. Due to the water, the porosity in the ITZ increases and the bond with the paste matrix is getting worse.

Another explanation deals with the weakest link theory. When the stress in the body reach the ultimate strength of the weakest member, the deformation localizes to this point and stress decreases. In case of the mortar, the fracture energy can increase (or have not to change) and the strength can be reduced.

4. CONCLUSION

The cement paste/mortar reinforced with carbon nanotubes directly synthetized on the surface of the cement grains exhibit comparable mechanical properties as the cement paste/mortar reinforced with the separately added carbon nanotubes as introduced in [8.]. Previous attempts to create nano-reinforced composite materials suffered from flocculation and improper dispersion of separately added nanofibers/nanotubes. The main advantage of the new method presents the elimination of the demanding CNT dispersion; now, the hybrid material can be intermixed directly with water and/or sand, creating strong and brittle composite similar to ordinary cement paste/mortar.

The decrease of compressive strength on CNT-reinforced mortar samples could be caused by the higher amount of water in the ITZ which was pushed out by the extremely hydrophobic carbon nanotubes. Preliminary experiments with high compacted (60 Mpa) mortar samples with the mixing w/c ratio 0.35 does not exhibit the compressive strength reduction. The future work will focus on the reduction of ITZ effect incorporating the CNT into the ITZ.

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