

CARBON NANOFIBER/CLINKER HYBRID MATERIAL AS A HIGHLY EFFICIENT MODIFICATOR OF MORTAR MECHANICAL PROPERTIES

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Abstract. Carbon nanofiber (CNF) / clinker hybrid material was prepared by a direct synthesis of CNFs on the surface of clinker particles in a fluidized bed reactor using acetylene and carbon dioxide gases at the temperature of 550 °C. This allowed us to achieve a good dispersion of CNFs in a clinker matrix and to prepare strong mortar composite. Optimal concentration of the CNFs to enhance mechanical properties of the mortar was found to be around 0.4 %, which led to more than 2.5-fold increase in the compressive strength.

1. Introduction

The world's production of cement has significantly increased in the recent years due to the growing construction demand. At the same time, there is a need to create a strong mortar by using composite materials based on cement. Due to their excellent mechanical properties, carbon nanofibers (CNFs) have been proposed to be used in various composite applications [1, 2]. Theoretical and experimental studies have indicated that CNFs exhibit Young modulus varying from 4 to 6 GPa and the tensile strength of around 0.2–0.3 GPa [3, 4]. Compared to carbon nanotubes (CNTs) that possess even better mechanical properties, CNFs have a couple of advantages: they are cheaper to produce and they have irregular form with carbon dangling bonds, which prevents sliding and can react and create bonding with a matrix. However, both CNTs and CNFs are very difficult to incorporate into a matrix material, since they easily form aggregates, which preclude obtaining improved properties of composite materials [5].

Preparation of a good dispersion of CNTs/CNFs is a very challenging task. A simple powder mixing procedure leads to a poor dispersion of the carbon nanomaterials in a cement matrix. Therefore Sanchez and Ince proposed to add silica fume to cement to increase the dispersibility of CNFs [6]. Also, it was proposed to disperse CNTs/CNFs in water using surfactants, which is a common way to introduce the carbon nanomaterials into polymers, and to add the prepared dispersion to cement [7-9]. However, most surfactants and additives can interfere with the hydration reaction of cement usually inhibiting cement setting and

hardening [10]. Another way to enhance the dispersibility of CNTs/CNFs is to functionalize them. Then, the formed carboxyl or hydroxyl groups attached to the surface of CNTs/CNFs during oxidation treatment can create bonding between a matrix material and carbon nanomaterials. Functionalized CNTs have been already proven to get bonded with cement hydration product [11-15], however, are very time consuming for the material preparation.

Recently, we have proposed a novel approach to get a good dispersion of CNFs in cement by growing CNFs directly on cement (clinker) particles [16]. We synthesized a cement hybrid material, wherein CNFs are attached to the cement particles, providing an exceptional dispersion of the carbon nanomaterial in the matrix. The material has been proven to increase 2 times the compressive strength and 40 times the electrical conductivity of the hardened paste [17, 18]. However, due to the amount limitations of the cement hybrid material it has not been yet examined to enhance the performance of mortar. Here, we report the results of the CNF growth on clinker particles in a fluidized bed reactor and investigation of mechanical properties of concrete made of the clinker hybrid material used as an additive to cement-sand mixture. It has been demonstrated 2.5-fold enhancement in the compressive strength.

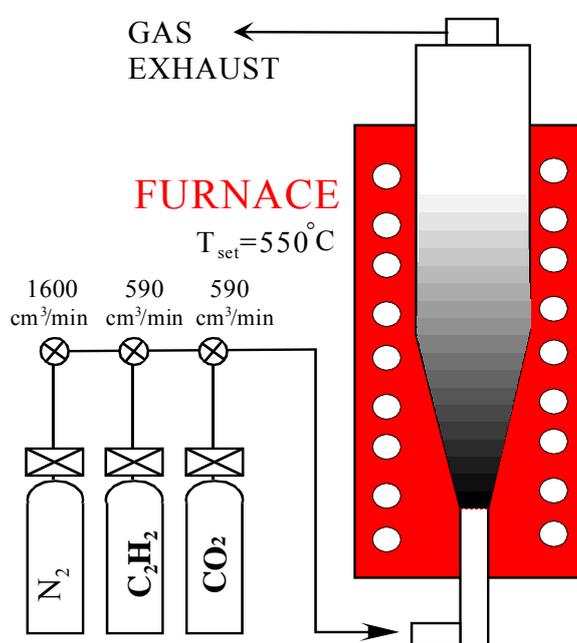


Fig 1. Schematic presentation of the fluidized bed reactor used for synthesis of CNFs on the surface of clinker particles.

2. Experimental results and discussions

The synthesis of CNFs on the surface of clinker particles was carried out in the experimental setup shown in Fig. 1. The reactor consists of a quartz tube inserted inside the vertical furnace with a heated length of 60 cm [17]. The quartz tube was conically shaped with a junction from internal diameters of 6 to 34 mm with the cone zone length of 20 cm. For one experiment, 50 - 100 g of well-ground clinker powder was filled up in the reactor. Then, 590 cm³/min of CO₂ and 590 cm³/min of C₂H₂ flows were introduced in the reactor. C₂H₂ was utilized as a carbon source, while CO₂ was used as a promoting agent, which role has been already discussed in our previous paper [18]. The nitrogen flow was gradually turned off during about 5 min after achieving the fluidization. After a certain period of growth time C₂H₂ and CO₂ were replaced by nitrogen and the reactor was cooled to room temperature. Typical

productivity of the final product was about 75 g/hour. The growth time was varied from 6 to 30 min to optimize the growth conditions.

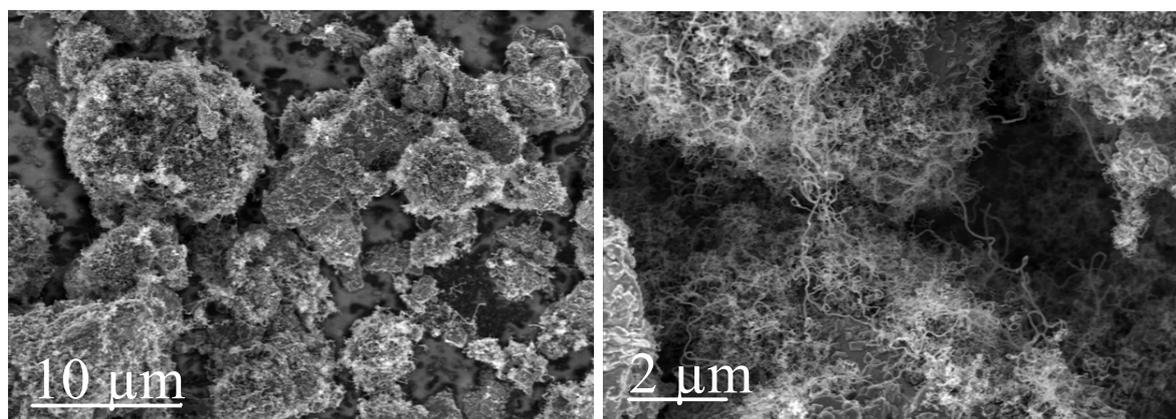


Fig. 2. SEM images of CNF/clinker hybrid material grown during 30 min.

Scanning electron microscope (SEM, Leo DSM 982 Gemini and JEOL JSM-7500FA) images of the samples synthesized during 30 min are shown in Fig. 2. As seen from the images CNFs form uniform and good coverage of clinker particle surface with an average length of about 10 μm . Transmission electron microscope (TEM Philips CM200 FEG) image of the product synthesized on the clinker particles revealed the CNF formation of about 30-50 nm in diameter, usually with catalytic particles at their ends (Fig. 3). Therefore, we could assume the tip growth mechanism of CNFs on the clinker particles, when CNFs grow on the catalyst detaching from the clinker surface.

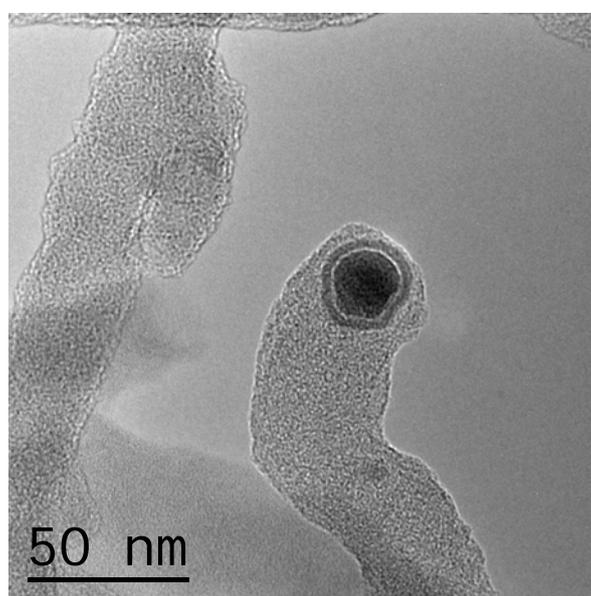


Fig 3. TEM image of the CNFs produced on the surface of clinker particles.

To determine the CNF concentration, three specimens produced with 9, 18 and 30 min growth time and plain clinker were examined by a thermogravimetric analysis (TGA, Netzsch STA 449C) in the temperature range of 20–950 $^{\circ}\text{C}$ under dynamic air atmosphere of

40 cm³/min. The first region, where the mass decreases at the temperature interval from 360 to 460 °C in TGA curves, corresponds to the burning of CNFs (Fig. 4). This was confirmed by SEM investigations (not shown) and visual observation of the color change of the CNF/clinker sample heated to 550 °C in air and then cooled to room temperature in a nitrogen atmosphere in the TGA device. The second stage of the TGA curve from 550 to 700 °C can be explained by decomposition of calcium carbonate and CO₂ release. Thus, the TGA results showed that the concentration of CNFs on clinker particles was varied from 1 to 5 %. The amount of the deposited CNFs on the surface of clinker particles depended on the growth time. The CNF mass increase has a liner dependence on the synthesis time (Fig. 5).

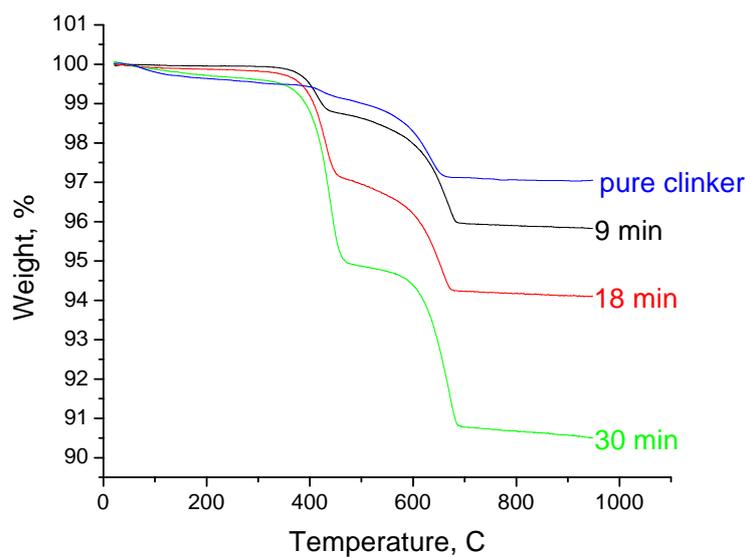


Fig. 4. TGA curves of CNF/clinker hybrid material produced with different growth time.

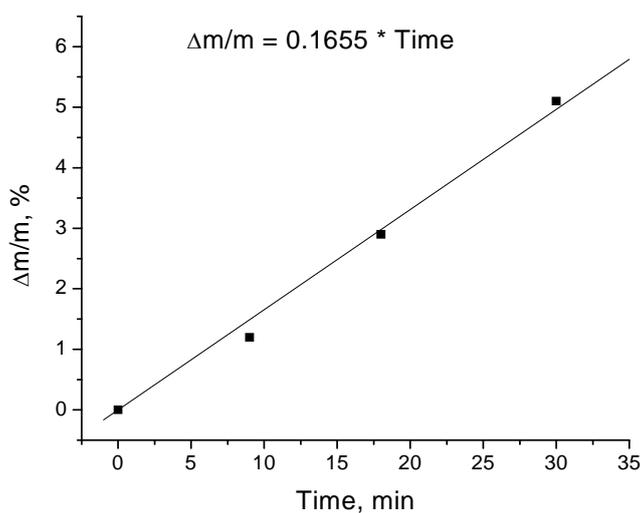


Fig 5. Kinetic dependence of a mass change of the CNFs produced on the surface of clinker particles.

Due to the high concentration of CNFs, the sample produced at the growth time of 30 min, which corresponds to the CNF concentration of 5 wt. %, can be utilized as a modifier

for the mortar preparation, similarly to the master batch in polymer composite materials. Therefore, one part of CNF-clinker and Portland cement mixture and three parts of sand (0.5 – 0.9 mm fraction) were well mixed. To prepare mortar the water/cement ratio was 0.4. The size of mortar beams was 40x40x160 mm³. In order to find the range of the CNF concentrations that are suitable for preparation of strong mortar, we used 7, 30 and 100 % of CNF-clinker hybrid material in Portland cement, which respectively correspond to 0.4, 1.5, and 5 % of CNFs in the cement. The results of flexural and compressive strength measurements of samples after 28 days curing in water are summarized in Table. As can be seen from the Table, the best results were obtained for the sample with the CNF concentration of 0.4%; compressive strength increased almost 3 times, whereas the flexural strength increase was not so significant. It is worth noting that the mechanical properties of the 5 % CNF sample deteriorated likely due to the aggregate formation and inhomogeneity in the composite matrix [20].

To check the reproducibility of the results and to find finer effect of the CNF concentration on the properties of mortar we prepared the second set of the samples with the CNF concentrations around 0.4 %: namely, 0.2, 0.4, and 0.5 %. As can be seen from the Table, the flexural strength did not considerably change, while the compressive strength of the sample with the CNF concentration of 0.4 % again revealed the most significant improvement; more than 2.5 times compared to the sample prepared without CNFs.

Table. Mechanical properties of concrete prepared by adding different samples of CNF/clinker composite (after 28 days curing in water).

Test number	CNF concentration, %	Flexural strength, MPa	Compressive strength, MPa
1	0	5.8	58
1	0.4	6.0	172
1	1.5	5.1	58
1	5.0	1.6	20
2	0	6.7	87
2	0.2	7.2	130
2	0.4	7.1	217
2	0.5	7.4	138

In order to understand the effect of the CNFs on mechanical properties in the mortar, we prepared and observed two CNF/clinker samples: after 1.5 hours curing in water to observe the nucleation stage of the hydration process and after 28 days curing in water to examine the microstructure of the mortar beams (Fig. 6). As can be seen from Fig. 6a the sample observed after 1.5 h hydration in presence of CNF/clinker composition revealed that the formation of hydration products took place also between the CNF network forming a tangled structure. After 28 days curing most of the CNFs are incorporated in the structure of the hydration products as can be seen from Fig. 6b.

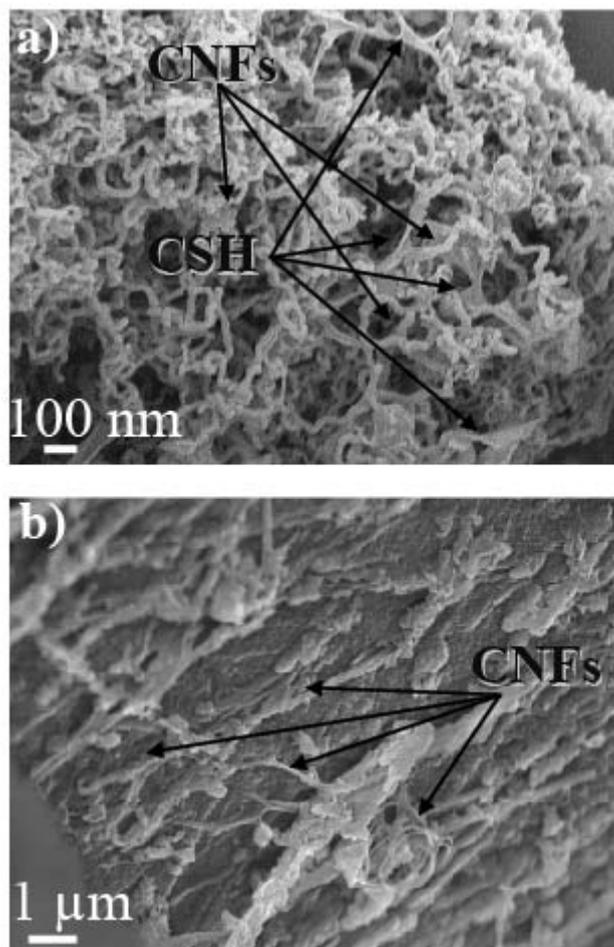


Fig 6. SEM images of hydrated CNF/clinker material: a) after 1.5 hour hydration process showing that the hydration products and CNFs form tangled structures; b) polished part of a concrete beam produced after 28 days curing in water showing that CNFs are completely incorporated in the concrete composite.

Let us discuss the role of the CNFs in the final mortar composite on the basis of our mechanical tests and the SEM observation. The significant improvement in the compressive strength of CNF/clinker mortar composite can be explained by formation of elastic CNF layers between cement particles and probably between cement and sand particles. The CNFs are responsible for spreading the stress between large numbers of intergranular contacts under compression. Additionally, it is known that CNFs slow down the rate of the hydration process [18], which is expected to result in the formation of CSH with better crystallinity and greater mechanical properties, which are important for the compressive strength enhancement. Therefore, in general the compressive strength should strongly depend on the quality of CNF dispersion in the cement matrix and CNF concentration.

It is important to note that under flexion the distribution of the stresses in the sample is non-uniform. The specimen starts to break at the weakest point of the most strained area and then the fracture propagates through the whole sample. The weakest places in the mortar are intergranular faces between sand particles and other components and also voids. It is important that the presence of CNFs does not affect these faces. Therefore, we did not practically observe the improvement of the flexural strength by introducing CNFs in the cement.

To the best of our knowledge, these significant improvement of the compressive strength is the highest reported so far obtained with the help of CNFs and CNTs. Up to now, the carbon nanomaterials added to cement matrix resulted in either decrease or rather small (up to 20 %) increase of the compressive strength [21-24]. It is believed that the main problem was in getting a good dispersion of the carbon nanomaterials in a cement matrix [18]. Therefore, our method allowed us to disperse CNFs homogenously in the cement providing suitable conditions for good mixing with the products during hydration process.

3. Conclusions

Clinker particles were utilized as a catalyst and as a support material for the synthesis of CNFs in fluidized bed reactor using acetylene and carbon dioxide gases at the temperature of 550 °C. This allowed us to prepare CNF/clinker hybrid material, wherein CNFs are attached to the clinker particles and provided a good dispersion of the carbon nanomaterials in the future matrix. Investigations of the mechanical properties of the mortar made of the CNF/clinker hybrid material mixed with Portland cement and sand revealed that the optimum CNF concentration was 0.4 % resulted in more than 2.5-fold increase in the compressive strength after 28 days curing in water. No significant changes in the flexural strength were observed. Therefore, the CNF/clinker hybrid material can be used as a hardening modifier for the preparation of mortar with enhanced compressive strength.

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