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## CARBON NANOTUBES INFLUENCE ON THE COMPRESSIVE STRENGTH OF CEMENT COMPOSITES

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### WPLYW NANORUREK WĘGLOWYCH NA WYTRZYMAŁOŚĆ NA ŚCISKANIE KOMPOZYTÓW CEMENTOWYCH

#### Abstract

Cement concrete is one of the most versatile building materials ever created. More and more often, microfibers and polymer or carbon nanofibers are added to concrete mix, causing beneficial changes in material properties. Nanotechnology, has only recently found its way into practical building applications and building materials, including concrete. The technological guidelines for the preparation of cement composites containing carbon nanoparticles are presented in the paper. The results of laboratory research concerning the impact of carbon nanotubes on the compressive strength of cement mortar is also discussed in this work.

*Keywords: carbon nanotubes, strength of cement mortar*

#### Streszczenie

Beton cementowy jest jednym z najbardziej uniwersalnych materiałów budowlanych, jakie udało się stworzyć człowiekowi. Coraz częściej obok tradycyjnych składników betonu dodaje się do mieszanki mikro- i nanowłókna polimerowe lub węglowe, które powodują zmiany właściwości tworzywa betonowego. Nanotechnologia, która dopiero od kilku lat na dobre wkroczyła w fazę praktycznych zastosowań w produkcji materiałów budowlanych, dotarła również do technologii betonu. W artykule przedstawione zostaną wytyczne technologiczne przygotowywania kompozytów cementowych zawierających nanocząsteczki węglowe oraz wyniki badań laboratoryjnych wpływu nanorurek węglowych na wytrzymałość na ściskanie zapraw cementowych.

*Słowa kluczowe: nanorurki węglowe, wytrzymałość zaprawy*

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### 1. Introduction

Nanotechnology is one of the most up-to-date and the fastest growing fields of science. Huge potential has been predicted for nanotechnology applications in construction [1]. Even minor improvements in materials and processes could bring large benefits. Nanotechnology development could lead to a completely different approach to the design and production of materials or structures with much improved energy efficiency sustainability and adaptability to changing environment.

The nanotechnology in construction roadmaps was developed in 2009 [2, 3]. Three original sectorial charts were described in [3] as follows:

Chart 1: Traditional Bulk Construction Materials – ‘top-down’ approach – existing material is improved through knowledge and modification carried out down at the micro-nano level (Fig. 1). Other material nano-development can be seen in [3] where the roadmap is given in detail.

Time:		5 years	10 years	20 years	25 years and later	Achievements
Steel						Bulk construction materials with highly improved properties and of least influence on environment
Concrete	low energy cement					
	novel, non-traditional binders					
	ductile cements & tougher concrete					
	nano-layers/coatings					
Ceramics, bricks, glass						
Bitumens, polymers						
Timber						

Fig. 1. Schedule of nano-development in bulk construction materials

**Chart 2: Buildings of Future** – the potential exploitation nanotechnology should lead to a much higher standard and much more environmentally acceptable and fully sustainable, building construction.

**Chart 3: Novel Construction Materials** – ‘bottom-up’ approach – materials of substantially altered properties and with much higher performance are ‘built’ or ‘assembled’ from the basic nano-scale constituents (molecular – atomic level); no health hazard; acceptable degree of sustainability harmless resources, environmentally harmless on global scale.

Nanotechnology is the study and design of matter on the molecular and atomic level. For the material to be considered of nanotechnology type, its structure must have at least one dimension from 1 to 100 nanometres in size.

Nanotechnology could be characterised as: the creation of nanomaterials, nanomodification of common building materials, study of the properties of nanostructure and identification and characterization of nanoscale structures. Almost all building materials can be modified with nanoparticles. Scientists use: nano-titanium dioxide, nano-silica nano-silver, nano-aluminium oxide, nano-zinc oxide, nano-iron oxide and nano-clay to improve building material properties.

Observing the use of nanotechnology in cement composites and describing the effect of hydrated cement phases, makes it easy to understand the relationship between structure and macro scale properties of materials [4, 5].

For the last decade, nanotechnology has been successfully applied to cement materials. It can enhance some of the traditional properties or introduce new capabilities of the material. An addition of a CNT additive to cement leads to an increase in amount of crystal hydrates formed in the cement paste and to change in their morphological structure [6]. The positive effect of carbon nanotubes on the elastic properties of cement stone is clearly visible at the macroscopic scale by using an ultrasonic device [7]. Previous research shows that the addition of carbon nanotubes can enhance the strength of cement matrix materials. It was found that small amount of effectively dispersed CNTs can significantly increase the flexural strength [8–10]. Even better results were obtained for compressive strength [6]. Other tests found that compressive strength decreases while the nanotubes were added to cement composites [11]. The porosity and pore size distribution results indicate the cement paste containing CNTs had lower porosity and a more uniform pore size distribution [8–10]. Nanomodified composites have a higher degree of stiffness C-S-H [10].

The main problem with the use of nanotubes is their tendency to agglomerate and low adhesion to cement paste. Because of its hydrophobic nature it is difficult to disperse the CNTs in cement matrix. A lot of different admixtures were used to obtain a homogenous dispersion of CNTs in aqueous solution and then in concrete mix [11, 12]. In order that CNTs have a beneficial effect on the mechanical properties of cement based composites, appropriate dispersion of CNTs is mandatory.

The aim of this paper is to investigate the possibility of using multi-walled carbon nanotubes Taunit-M in cement matrix materials and to study its influence on compressive strength of cement mortar.

## 2. Experiments and results

### 2.1. Materials

A commercial cement CEM I 42,5R conforming to the requirements of Polish Standard PN-EN 197-1 was used as a binder material. The chemical composition and properties of the cement is summarized in Table 1. The amount of binder was constant at the value of 525 kg/m<sup>3</sup>.

Multi-walled carbon nanotubes “Taunit-M” (CNTs) were used as nano additives. It was a powder form. The nanotubes are quasi one-dimensional, nanoscale, filamentous formation of polycrystalline graphite cylindrical shape with an internal channel (Fig. 2). They are obtained by chemical vapour deposition (CVD) by catalytic pyrolysis of hydrocarbons. Properties of the CNTs are given in Table 2. The content of CNTs was 0.00 %; 0.06% and 0.12% by weight of cement respectively.

**Chemical compositions and physical properties of OPC**

<i>Parameter</i>	
Initial setting time (min)	160
Final setting time (min)	220
Specific surface (cm <sup>2</sup> /g)	3800
Soundness (mm)	0.9
Compressive strength (MPa)	
• 2 days	28
• 28 days	52
Loss on ignition (%)	1.64
Insoluble (%)	0.77
SO <sub>3</sub> (%)	2.87
Cl (%)	0.08

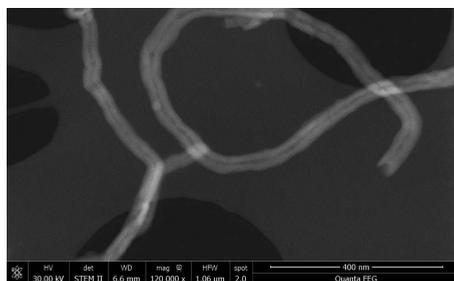


Fig. 2. HAADF STEM image of CNTs “Taunit-M”

**Properties of the CNTs used – “Taunit-M”**

<i>Parameter</i>	
External diameter (nm)	8–15
Internal diameter (nm)	4–8
Length (μm)	2 and more
Total amount of impurity (%) (after purification)	up to 5 (up to 1)
Bulk density (g/cm <sup>3</sup> )	0.03–0.05
Specific surface (m <sup>2</sup> /g)	300÷320 and more
Thermal stability in air (°C)	up to 600

A new generation superplasticizer – range water reducer, based on modified polycarboxylate (SP) was used for facilitating in dispersing CNTs (Fig. 3). Fine aggregate natural rinsed sand was used. The maximum diameter of the aggregate was 1 mm.

Distilled water was used to prepare the mortar mixtures.

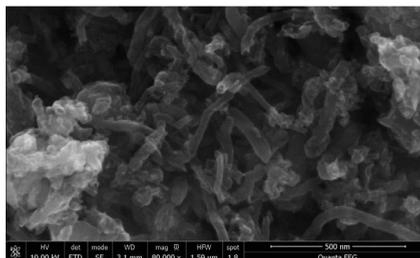


Fig. 3. SEM image of CNTs agglomerations

## 2.2. Concrete mixtures

Tests were carried out on cement mortar specimens prepared for mixtures with two different values of CNTs content: 0.06% and 0.12% related to cement mass. Similar tests were carried out on unmodified control specimens.

The cement content in all mixtures was  $525 \text{ kg/m}^3$ . The water to cement ratio (w/c) in the tested mortars had the value of 0.45. To achieve a plastic consistency of mixtures and for facilitating in dispersing CNTs superplasticizer (SP) was used. The amount added was 1.0% the weight of cement. The amount of aggregate was constant and in each composition was  $1580 \text{ kg/m}^3$ .

## 2.3. Preparation of mortar mixtures

At first aqueous solution was prepared. The superplasticizer was initially mixed with 50% of proper amount of distilled water. Then the CNTs were added and the solution was stirred for 21 minutes using ultrasonic homogenizer SONICS VCX-130.

Ultrasonication method previously prepared solution (Fig. 4) was combined with the rest of water and then with the binder. The cement paste was mixed for 10 seconds then the sand was added and all ingredients of the mortar were stirred for 7 minutes.

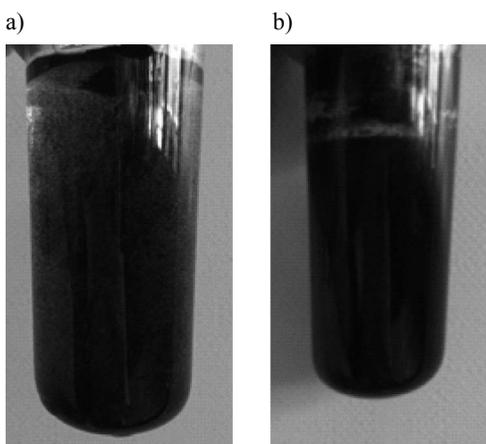


Fig. 4. Aqueous solution of CNTs: a) before ultrasonication process, b) after ultrasonication

## 2.4. Formation and test

The mortar was cast in cylinder shaped moulds (diameter  $\phi = 42$  mm, height  $h = 42$  mm) and compacted by vibration. The specimens were stored at temperature of  $40 \pm 2^\circ\text{C}$  and relative humidity (RH) above 90% until test time. They were tested for compressive strength after 7 and 28 days of curing. The number of samples in each test was 3.

## 3. Test results and discussion

The variation of compressive strength with curing time of cement mortars in dependence on CNTs content is presented in Fig. 5. After 7 days of curing, the carbon nanotubes content caused significant decrease in compressive strength. The compressive strength is inversely proportional with the CNTs content in mixture. The CNTs mortar with the amount of 0.06% by weight of cement achieved 90% of compressive strength of controlled specimens but the mortar with 0.12% of nanoparticles achieved only 84%.

After 28 days of curing the significant increase in compressive strength in comparison with the 7 days strength was observed (Fig. 5). Between 7<sup>th</sup> and 28<sup>th</sup> days the compressive strength increased about 17.7% for mortar without nanotubes and 68.5% or 47% for mortars with 0.06% or 0.12% of CNTs, respectively.

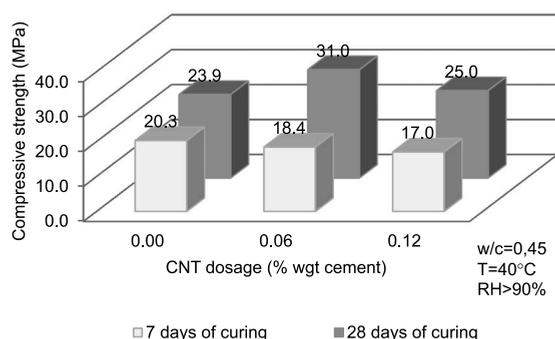


Fig. 5. Effect of CNT dosage and time of curing on compressive strength of cement mortar

The beneficial effects of CNTs on the strength of cement mortars can be also observed. The compressive strength of mortar with 0.06% and 0.12% of CNTs content were 29.7% and 4.6% higher than the controlled mortar, respectively.

## 4. Conclusions

The present investigation has shown it is possible to design and use nanomodified concrete incorporating nanomaterials and nanoproducts which leads to an improvement in the materials characteristics or give new properties to the considered materials. The biggest

problem in the preparation of cement composites containing CNTs is their proper dispersion in the mass.

Ultrasonication method helps to resolve the problem uneven dispersion and tendency to aggregation of carbon nanotubes. The positive effect of nanoadditive was found. It was almost 30% increase in strength for mortar with CNTs in amount of 0.06% by cement mass. The introduction of CNTs into cement mortar caused a decrease in the 7-day compressive strength. However, the significant increase in strength (even more than 68% for CNTs content 0.06% by weight of cement) was observed between 7<sup>th</sup> and 28<sup>th</sup> days of curing.

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