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Procedia Engineering 151 (2016) 157 – 161

**Procedia  
Engineering**[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)

International Conference on Ecology and new Building materials and products, ICEBMP 2016

## Electric conductivity changes in geopolymers with added carbon nanotubes

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### Abstract

By incorporation of nanotubes to the current composite materials, their properties can be significantly improved. Carbon nanotubes can act as filler, which minimizes the air gaps content in the matrix. The denser structure positively affects the physical and mechanical properties of the whole composite. The paper deals with alkali-activated materials (AAM) based on finely-ground granulated blast furnace slag modified by carbon nanotubes. Prismatic samples of this type of AAM were prepared with addition of 0.1 – 0.4 wt. % of carbon nanotubes (with 0.1 % step). The change of electrical parameters (electrical capacity, relative permittivity, real and imaginary impedance component) was observed. The obtained results indicate that the absolute value of the impedance decreases with increasing amount of carbon nanotubes and relative permittivity shows the general increase. The results may contribute to further research and development of alkali-activated systems, focusing on practical applications in construction.

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Peer-review under responsibility of the organizing committee of ICEBMP 2016

**Keywords:** Electrical measurements; geopolymer structure; dielectric losses; loss factor; permittivity; carbon nanotubes

### 1. Introduction

The results show that the application of carbon nanotubes in material results in increased strength, elasticity and overall durability [1,2]. Nanotubes exhibit a low density (1.3–1.4 g·cm<sup>-3</sup> by the type of carbon nanotubes), high thermal conductivity (1 750–5 800 W·m<sup>-1</sup>·K<sup>-1</sup>) and through delocalized bonds along the carbon layer also has

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excellent electrical conductivity. Carbon nanotubes are considered as potential substitutes for reinforcement in composites, because they have mechanical, chemical and thermal properties superior to traditional fibers [2].

Alkali-activated materials, so called geopolymers, represent a specific group of inorganic cement-free materials. Formed by reaction of latent hydraulic substances or pozzolana (granulated slag, fly ash, metakaolin) with a suitable activator. Activators may be used as solutions of soluble compounds of alkali metals, especially sodium and potassium, in particular carbonates, hydroxides or silicates. The product of this activation are hydraulic binders which are suitable, after addition of water, for the formation of composite materials with excellent utility properties [3]. Alkali activated materials can practically serve as an alternative to conventional building materials, especially cement based concrete, but thanks to its parameters can be applied in a number of other disciplines (eg. in the restoration of monuments, etc.). Despite the fact that studies of alkali-activated materials have been ongoing since the sixties of the last century, their potential is still exploited only in sporadic scale.

Indisputable advantage of the use of alkali-activated materials are economical and ecological. These materials are important because they can utilize the secondary raw materials, exhibiting the latent hydraulicity or pozzolanic activity, especially high-volume by-products of metallurgy and energy. Preparation of the alkali-activated binders and composites takes place at normal or slightly elevated temperatures, does not require previous firing of the raw materials (as in the case of Portland clinker) or consolidation by sintering at high temperatures (connected with the formation of CO<sub>2</sub> from combustion processes), and does not consume raw materials. The advantage of alkali-activated materials is also the possibility of widespread use often non-standard fillers which are used in the production technology of concrete.

This paper presents the basic electrical properties of laboratory prepared alkali-activated composite materials based on finely-ground granulated blast furnace slag with the addition of different amounts of carbon nanotubes.

To make use of electrically-oriented test methods, it seems appropriate to use admixture of carbon nanotubes, which increases the conductivity of the test specimens. The increased conductivity will increase measurability and leveraging inter alia, methods of impedance spectroscopy. The admixture of carbon nanotubes is in the tenths of a percent of the total weight of the sample and can be detected by measuring for example the percolation threshold. In further research, we want to compare results of measured samples with added graphite, carbon black and carbon fibers (as the economic aspect must be also taken into consideration).

## 2. Materials

Several kinds of raw materials were used to prepare the samples. The function of the binder takes alkali-activated form of finely ground granulated blast furnace slag. Activation was carried in waterglass solution, the silica modulus was treated with 50 % sodium hydroxide solution to  $M_s = 2,0$ . As filler was used norm-test sand and carbon nanotubes in different amounts for different sets. The partial blend compositions are described in Table 1.

In order to prepare the aqueous dispersions, the procedure prescribed by the producer was followed. MWCNT (Multi Walled Carbon Nanotubes) pellets were dissolved in hot water and dispersed bundles of MWCNTs were further disintegrated by mechanical homogenizer (3 h at 14000 rpm).

For each of the five mixtures 3 samples of dimensions 20×20×95 mm were produced. The individual results are compared with a reference sample.

Table 1. Recipes for individual mixtures with geopolymer.

Ingredients	Ref.	0.1 % wt MWCNT	0.2 % wt MWCNT	0.3 % wt MWCNT	0.4 % wt MWCNT
Slag (g)	140	140	140	140	140
Waterglass (g)	28	28	28	28	28
Sand (g)	140	140	140	140	140
MWCNT (mg)	0	140	280	420	560
Water (ml)	57	57	57	57	57

### 3. Experimental setup

Testing: Prepared test bodies (Table 1) were characterized by impedance spectroscopy. Function waveform generator Agilent 33220A and dual-channel oscilloscope Agilent 54645 were used in the experiment. These instruments were assembled according to the proposed scheme for fully automated measurement [4–8]. For communications equipment and data processing software was created in programming environment C++ Builder. Electrical values were measured for frequencies in the range from 40 Hz to 1 MHz. Monitored variables were: loss factor  $\tan \delta (f)$ , the imaginary component impedance  $Z (f)$ , the real component of impedance  $\text{Re } Z (f)$  electrical capacity  $C$  and calculation of the relative permittivity of the selected frequency spectrum. In order to perform impedance analysis it was necessary to place the samples between brass electrodes with a surface corresponding test specimens ( $20 \times 95 \text{ mm}$ ) [4–8].

### 4. Results and discussion

AC resistance (Fig. 1a) of the samples without MWCNT (REF) and with concentration of MWCNT from 0.1 to 0.4 % was detected for the frequency of 40 Hz to 1 MHz. The highest values of  $\text{Re } (Z) 7 \times 10^5 \Omega$  were observed for the reference sample, other samples had lower  $\text{Re } (Z)$ . A special case is the MWCNT sample with 0.1 % concentration, which has in the first half of the frequency band lower AC resistance and in the second half values blended with the values of the reference sample. The values of the real component impedance decreases in all samples together and approaching the units  $\text{k}\Omega$ . The presence of carbon nanotubes in the sample creates a conductive path, which corresponds to a reduction of electrical resistance for samples with higher concentration of MWCNTs, such phenomenon can be observed in the graph in Fig. 1a, were measured values  $4 \times 10^5 \Omega$ , was found a downward trend values for samples MWCNT 0.2 to 0.4 % slightly overlap across the spectrum. Measurement uncertainty as a result of blending can be ruled out, even in 1 MHz observed deviation from the curve retention sample, seen in a logarithmic coordinate system on both axes. Stopping the increase of the conductivity with increasing concentration of the MWCNT may be due to the real conditions of mixing fine MWCNT into fresh mixture geopolymer when tubes clustered together and thus are not uniformly distributed in the walls of the sample, which are subsequently enclosed with the conductive plate electrodes. A similar result will be broken into smaller pieces MWCNT, again as a result of mixing.

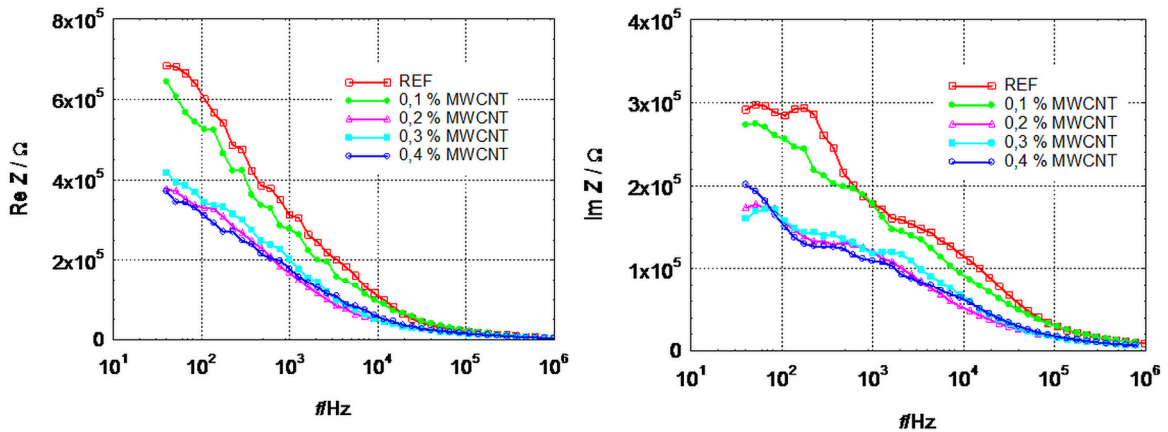


Fig. 1. (a) graph of the real part of the impedance at the frequency; (b) graph of the imaginary part of the impedance at the frequency.

For the imaginary part of the impedance versus frequency (Fig. 1b) observed similar trends of waveforms and levels curves, beginning of the reference sample with the largest values of  $3 \times 10^5 \Omega$ . Further value declines with increasing concentration of MWCNT. At 1 MHz approach each other, the impedance values achieved  $6 \times 10^3 \Omega$ , but from the last value of the reference sample differ appreciably.

Electric capacity of samples for concentration used MWCNT exhibits an increase of approximately twice that of the reference sample (Fig. 2a). Results for MWCNT with 0.1% reported again approaching the capacity of the reference sample in the entire frequency spectrum. The increase electric capacity due to impurities MWCNT due to the ability to store an electrical charge, whether in the form of free media or creating dipole elements.

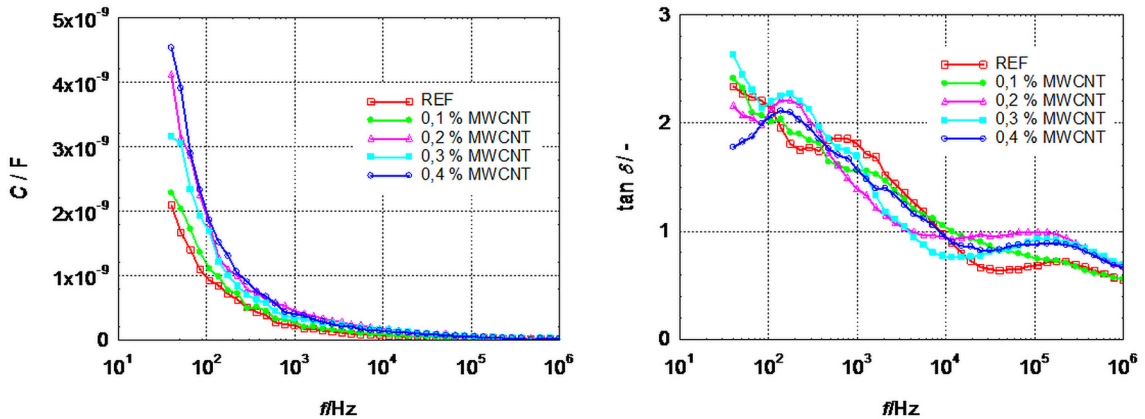


Fig. 2. (a) Dependence of electrical capacity on the frequency; (b) Dependence of loss factor on the frequency.

The observed spectra of dissipation factor (Fig. 2b) differ from the commonly observed dependence cementitious materials. Curve dissipation factor of the reference sample includes one peak around one kHz, and other frequencies around  $2 \times 10^5$  Hz. For ingredients MWCNT 0.1% this maxim cease curve on a downward trend, adequate conduction losses. Additions of 0.2 and 0.3 % MWCNT is to create polarization maxima, but in a region around 160 Hz and  $10^5$  Hz. Curve 0.4% MWCNT is compared to the previous significantly lower only to frequencies of 100 Hz, then the previous two rather adheres in the central part of the spectrum values are slightly higher, but again this further blending.

The electrical relative permittivity calculated for the frequency of 1 kHz acquired values from 250 to 550 (Fig. 3). To MWCNT concentration of 0.2% grew to the maximum, at concentrations of 0.3% had a decrease and subsequent slight increase to 0.4% MWCNT.

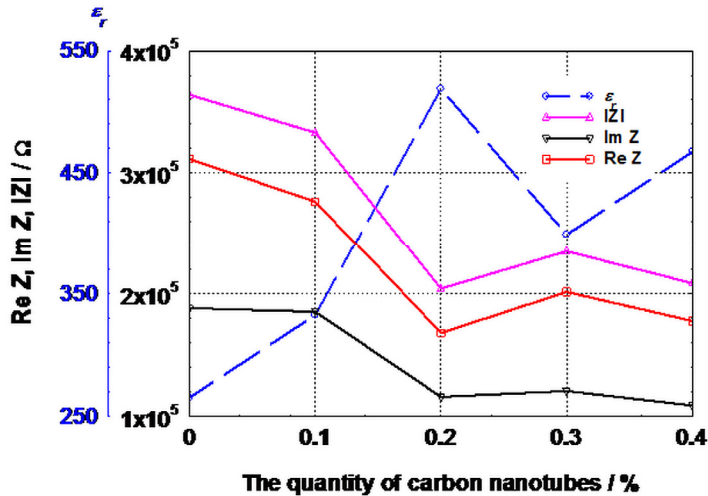


Fig. 3. Values of relative permittivity and impedance components of the reference frequency of 1 kHz.

The values of the two components of the impedance including the size of the absolute value of impedance show a decrease with increasing concentration, which can be expected, but for concentrations of 0.3 and 0.4%, there was a slight increase relative to the point MWCNT 0.2%.

Table 2. Electrical parameters of specimens, measured with a reference frequency of 1 kHz.

	$\epsilon_r$ (-)	Re Z (k $\Omega$ )	Im Z (k $\Omega$ )	Z  (k $\Omega$ )	C (pF)
REF	265.5	311.539	188.459	364.106	228
0.1 % MWCNT	332.7	276.723	185.487	333.138	286
0.2 % MWCNT	518.9	168.162	115.939	204.255	446
0.3 % MWCNT	399.6	201.519	120.798	234.951	343
0.4 % MWCNT	467.4	177.982	108.904	208.657	401

## 5. Conclusion

Based on the observed unexpected abnormalities in the trends of the impedance curves it can be assumed, that during the incorporation of the MWCNT into the geopolymer mixture, the breakage of nanotubes occurred at higher concentrations so they are not contiguous enough to create conductive tracks. Thus the samples exhibit lower conductivity than it was expected. However, the absolute value of the impedance decreases with increasing amounts of MWCNT fibers and relative permittivity indicates the general increase.

## Acknowledgements

This paper has been worked out under the project GAČR No.16-00567S and under the project No. S-16-2967 supported by Faculty of Civil Engineering BUT.

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