Self-sensing performance of metakaolin geopolymer with carbon nanotubes subjected to repeated compressive loading

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Abstract. Alkaline activated binders showing enhanced piezoresistive properties have recently attracted increased interest in research of their application in smart self-sensing components. This study is focused on metakaolin geopolymer mortar doped with 0.05 and 0.10% carbon nanotubes, a conductive filler that effectively increases electrical conductivity without considerable deterioration of mechanical properties. Self-sensing performance of composites incorporated with electrodes and attached strain gauge was tested during different regimes of compressive loading cycles with continuous monitoring of strain and resistivity. Although the differences in sensitivity and repeatability were observed, all samples including the reference material have shown good response to applied loading.

1. Introduction

Geopolymers are advancing inorganic binders prepared by alkaline activation of natural or manufactured source materials with prevailing aluminosilicate content [1]. Resulting geopolymeric binders feature highly coordinated microstructure and superior material properties that draw increased research interest in last decades. Apart from superior mechanical performance that have already proven themselves in many structural applications, geopolymers can exhibit exceptional durability, thermal resistance, and lower environmental impact in comparison with traditional cementitious binders [2]. Moreover, the certain material characteristics, different from the ones of OPC open new possibilities for advanced multifunctional geopolymeric composites [3].

The introduction of conductive fillers represents a common approach towards concrete with additional functionalities because enhanced electrical properties can provide a potential for designing elements with self-sensing, self-heating or electromagnetic shielding abilities [4]. Initial attempts in development of self-sensing concrete referring to a material able to detect alterations of its own structural health dates back to 90s. Structural health monitoring in self-sensing structures is performed via measuring the electrical resistivity that can reflect load induced mechanical strain and possible defects but also the external ambience conditions. Such solution of structural element being continuously self-monitored can serve as an alternative to currently used strain gauges that are expensive and ineffective in use [5]. In order to increase the concrete conductivity, various metal or carbon admixtures are used to establish functional conductive network within the composite and improve its self-sensing performance. The most common conductive fillers include carbon fibres, carbon nanotubes, graphite powder, carbon black, steel fibres or graphene [5][6].

Unlike poor conductivity of plain OPC, geopolymers and other alkaline activated materials, especially metakaolin and slag-based binders, exhibit higher conductivity ascribed to increased availability of mobile hydrated alkali cations in the pores of the geopolymeric structure [7] and the presence of Fe [8]. Piezoresistive behaviour of geopolymers described by Lamuta et al. [9] was later confirmed in experimental studies that revealed their applicability for the purpose of self-sensing measurements even without the use of conductive filler [8]. Nevertheless, the conductivity of geopolymers with/without conductive fillers vary greatly and the application of such admixtures remains an effective means to achieve convenient response in self-sensing tests and prevent conductivity loss at completely dry matrix [10].

Carbon nanotubes (CNTs) are single- or multi-walled tubular structures formed by rolling a sheet of graphene (carbon atoms in honeycomb lattice) into a tube with high aspect ratio. CNTs exhibit superlative mechanical properties (flexural strength, Young´s modulus) and excellent electrical behaviour [11]. The key issue of their applicability in self-sensing materials is the uniform distribution within the matrix, well dispersed CNTs result in significantly enhanced electrical performance in spite of very low concentrations usually not exceeding 1% wt. [12]. Alkaline solution used for geopolymer synthesis serves as a surfactant and facilitates the dispersion of CNTs. Besides, the presence of inert nanofillers in geopolymers (CNTs and graphene) contributes to refined pore microstructure of the binder hence improving its durability while acting as a microfiller and nucleation seeds for initial geopolymerization reactions [13]. Higher CNTs dosage is associated with inevitable agglomeration that can increase binder porosity and decrease mechanical performance, surpassing the threshold has rather impact on mechanical than electrical properties. Regarding the contribution to piezoresistive effect, CNTs enhance electrical conductivity and considerably improve the sensitivity in testing of self-sensing performance indicated by gauge factor (GF). Geopolymers doped with CNTs are characterized by much higher GF than cementitious binders incorporated with any type of conductive filler [12].

This paper deals with self-sensing performance of metakaolin geopolymers doped with CNTs subjected to repeated compressive loading. Experimental results are discussed in relation to strain and fractional change in resistivity during loading cycles. Fractional change in resistivity ((R□R0)/R0) is used to report sensitivity and repeatability in self-sensing performance. Moreover, it is an indicator of plastic/elastic deformation development during loading cycles.

2. Experimental part

2.1. Materials

The major source material for geopolymer preparation was metakaolin Mefisto K05 (České lupkové závody, a. s.) with predominant aluminosilicate content (55.01% SiO_2 and 40.94% Al_2O_3). Alkaline activator solution combined sodium silicate and 30% NaOH solution, standardized quartz sand with a maximum grain size of 2.5 mm was used as fine aggregate. Agglomerate powder of carbon nanotubes Graphistrength® C100 was supplied by Arkema, the solid concentrates were dispersed in hot water to prepare 2% CNTs solution. CNTs concentration in mortars was 0.05 and 0.10% by weight.

2.2. Specimen preparation

Metakaolin mortars were prepared in a standard planetary mixer according to following steps. At first, waterglass, NaOH solution, 2% CNTs solution and water were mixed to form a homogeneous suspension. Then metakaolin was added and mixed properly until well combined into a smooth paste. Finally, all fractions of fine aggregate were added. Compositions of all tested mortars are given in table 1.

Fresh mortars were cast into cubic moulds (100 × 100 × 100 mm) and incorporated with four copper mesh electrodes with dimensions 80 × 120 mm. Regular 20 mm distance between electrodes was assured by waterproof plywood board. Specimen were then covered with a plastic foil and left to set under laboratory conditions. Demoulded samples were wrapped in PE foil and stored in laboratory till the age of testing.

Table 1. Mix design proportions of geopolymer mortars.

	REF	CNT0.05	CNT0.10
Metakaolin (g)	900	900	900
Waterglass (g)	748	748	748
30% NaOH (g)	83	83	83
Sand (g)	2700	2700	2700
2% CNT solution (g)	-	22.5	45
Water (g)	103	80.5	58

Fresh mortars were cast into cubic moulds (100 × 100 × 100 mm) and incorporated with four copper mesh electrodes with dimensions 80 × 120 mm. Regular 20 mm distance between electrodes was assured by waterproof plywood board. Specimen were then covered with a plastic foil and left to set under laboratory conditions. Demoulded samples were wrapped in PE foil and stored in laboratory till the age of testing.

2.3. Testing methods

Compressive loading cycles were performed in a multipurpose electromechanic testing machine LabTest ® 6.250 (Labortech) allowing to achieve maximum 250 kN loading force. The repeated loading was carried out perpendicularly to electrodes configurated in a standard serial arrangement. We defined two different courses of linear loading: a) 10 cycles with constant amplitude (10 kN, 300 N/s); b) 30 loading cycles with increasing and decreasing amplitude (7–35 kN, 500 N/s). The applied load took place within the elastic region of the material and did not exceed 25% of the ultimate failure load.

Electrical resistance was measured under AC using a sinusoidal signal generator Agilent 33220A and two multimeters Agilent 34410A. The generated signal was brought to outer electrodes while the inner ones were used to measure the output voltage. The electrical resistance of the measured specimen was calculated from the electric current flowing through the exact resistance R and the voltage that was measured separately on the test sample using Ohm's law, taking into account the internal resistance of the voltmeter. The input frequency and voltage values were 1 kHz and 5 V, respectively. In order to monitor the longitudinal strain, strain gauges were attached to the sides of each specimen.

3. Results and discussion

3.1. Linear compressive loading with constant amplitude (10 cycles)

The first phase of self-sensing performance testing consisted in 10 linear compressive loading cycles with constant 10 kN amplitude. Longitudinal strain measured by the strain gauge in µm/m is shown in Figure 1 (a). We can see that the deformation rates of REF and CNT0.05 samples was comparable around 60 µm/m while the longitudinal strain of CNT0.10 was more than twice higher. Maximal strain of reference sample was slightly decreasing with each loading cycle while the highest deformation of CNT-doped samples was consistent.

Piezoresistive behaviour was observed at all samples, as the changes of loading force are reflected by the change in fractional resistivity in Figure 1 (b). Response of CNT samples were very similar, fractional change in resistivity was growing during the whole experimental course. Increasing resistivity refers to permanent structural defects formed within the binder microstructure causing the interruptions of conductive pathways. Fractional resistivity of reference sample was gradually decreasing but fluctuating in almost constant range, thus featuring better repeatability. Results achieved in self-sensing experiments of alkaline activated slag doped with carbon fibers [13] lead to similar outcome with the formation of microcracks and no improvement of self-sensing performance. On the other hand, 10% graphite [14] or 0.5% carbon black [15] improved the repeatability and sensitivity of fly ash geopolymer specimens during loading with constant amplitude, carbon black was a suitable admixture with high effectivity in low concentration and no harmful impacts on the mechanical performance of geopolymer matrix.

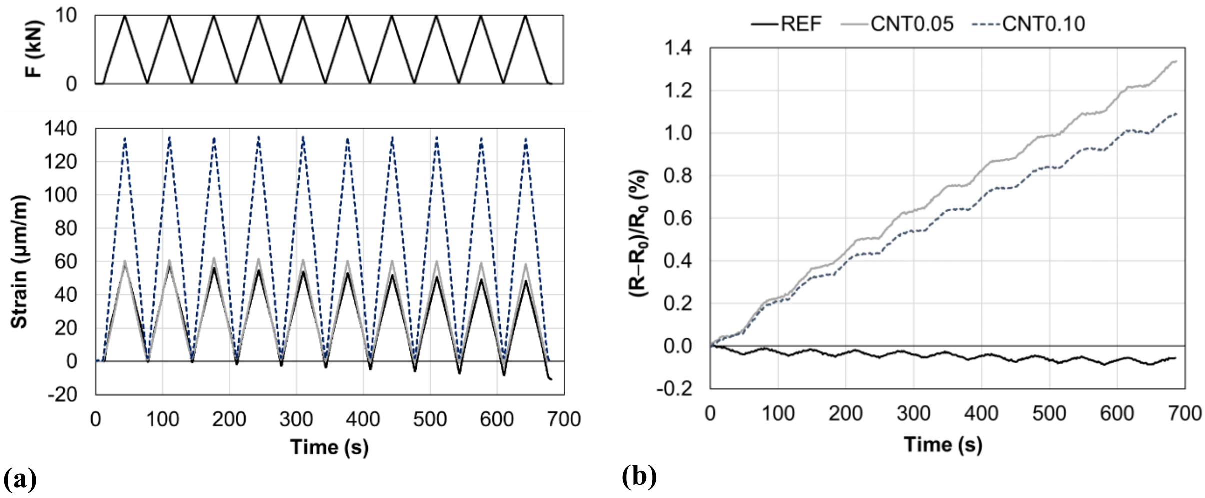


Figure 1. Specimens response during linear compressive loading with constant amplitude: (a) longitudinal strain, (b) fractional change in resistivity (self-sensing performance).

3.2. Linear compressive loading with variable amplitude (30 cycles)

Linear compressive loading with variable amplitude was performed in 30 loading cycles with an amplitude 7–35 kN. During this loading regime, CNT0.10 sample again reached the highest strain values, strain of CNT0.05 was comparable with REF (Figure 2). There were minor alterations in strain peaks with successive loading cycles.

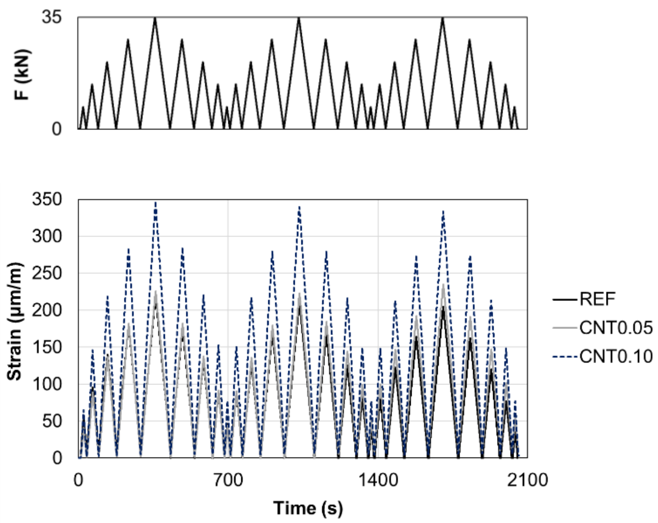
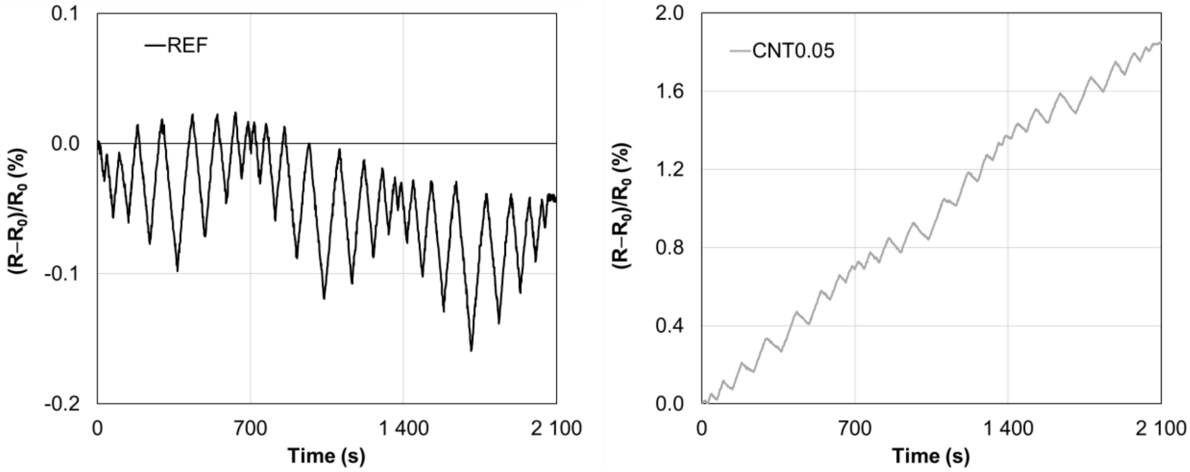


Figure 2. Longitudinal strain during linear compressive loading with variable amplitude.

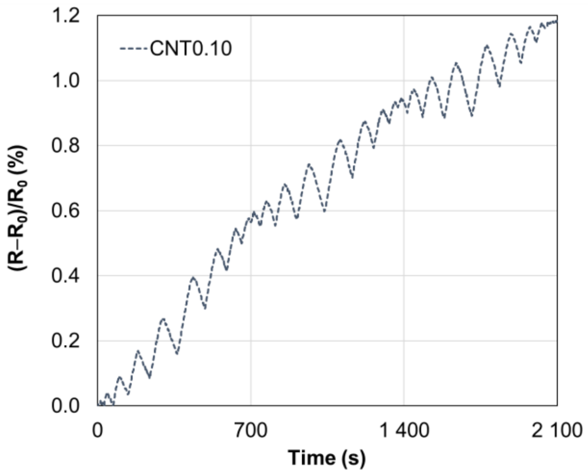
Self-sensing performance of geopolymers is shown in Figure 3 that displays the fractional change in resistivity response during the loading course. Samples with CNT content were again characterized by resistivity increasing with time, i.e. the irreversible plastic deformation. Similarly, to results in the previous chapter focused on loading force with constant amplitude, CNT0.05 suffered higher resistivity increment than CNT0.10. Increased strain levels of samples with CNT observed in this study are in a contrary of published papers reviewed in **Chyba! Nenašiel sa žiaden zdroj odkazov.** that mostly reported improved elastic modulus of CNT-doped mortars.

Fractional change in resistivity of all samples is displayed in figure 3. Response of REF sample (figure 3 (a)) corresponded well with the repeated loading cycles. There were observed minor changes of total resistivity, the sensitivity was around 0.10–0.15% at maximum loading force. The possible benefit of CNT modification to enhanced sensitivity in self-sensing tests was not established due to continuous resistivity growth (figure 3 (b), (c)), sample CNT0.05 exhibited the less favourable self-sensing performance. On the other hand, REF sample featured very good reproducibility and repeatability.

Application of CNT in this study did not lead to anticipated contribution to self-sensing performance under compressive loading, superior properties were observed in case of geopolymers with graphite [14] or carbon black [15] admixture. Even though the fractional change in resistivity exhibited higher peaks in corresponding loading cycles, these benefits were outbalanced by increasing resistivity.



(a) **(b)**



(c)

Figure 3. Self-sensing properties during linear compressive loading with variable amplitude: (a) reference material (REF), (b) sample CNT0.05, (c) sample CNT0.10.

4. Conclusions

The objective of this study was to determine the self-sensing performance of metakaolin geopolymer mortars doped with CNT. Reference material and specimens with 0.05 and 0.10% CNT, respectively, were each subjected to two series of compressive loading cycles with constant/variable amplitude. Measurements of corresponding change in resistivity response have shown that all samples exhibit good self-sensing performance but CNT-doped specimens suffered increasing resistivity related to permanent deformations. The performance of reference material was thus better in repeatability. Research of the mechanical and electrical properties influencing the self-sensing performance will be further studied in following experiments, ex. during loading till fracture.

5. References

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