Metakaolin/carbon black geopolymer with enhanced electrical properties

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Abstract. Alkali-activated binders represent a promising material for composites with self-sensing properties both for their lower environmental impact and ability to transfer the electric charge through ionic mobility. Metakaolin geopolymers with carbon black conductive admixture up to 4% were produced to test their electrical properties, mechanical properties and microstructure. Electrical capacitance, resistance and relative permittivity were determined via impedance spectroscopy analysis. Notable enhancement of all mentioned electrical parameters was registered from 2% carbon black content, especially at lower frequency range. Another carbon black addition was rather unreasonable due to only slight improvement in electrical properties but significant drop of compressive strength and unfavourable changes in pore volume and binder microstructure determined by mercury intrusion porosimetry and electron microscope.

1. Introduction

Intrinsic self-sensing concrete is a novel type of construction composite capable to serve both as the structural material and a sensor monitoring its own stress, strain or damage occurrence. The self-sensing property is related to changes in electrical conductivity and other parameters that are affected by mechanical loading, temperature and other external stimuli. Concrete incorporated with functional filler, for instance carbon fibres, carbon nanotubes, carbon black, graphite powder or steel fibres, forming the conductive network within the matrix, thus does not require additional monitoring devices that are in most cases expensive, less effective and limited in durability [1]. Apart from self-sensing, conductive composites can be applied in various advanced engineering solutions including modern traffic detection systems, self-heating concrete for deicing and heating or cathodic protection of steel [2]. Especially carbonous materials improve the concrete ability of electromagnetic shielding [3].

Alkali-activated binders drew considerable attention in present efforts to search for an alternative binder to traditional Portland cement production being one of the major sources of CO₂ and other pollutants released into the atmosphere [4]. Emissions related to their production can be similar or a way lower comparable to cement, maximal use of local and waste materials along with the lowest amount of alkaline activator needed represent an applicable approach in their wider adoption in practice [5]. The technology is based on the reaction of highly reactive aluminosilicate precursors, frequently slag, fly ash, metakaolin and other products or natural materials, with alkaline activator solution. A strongly alkaline environment causes dissolution of the source materials and formation of new binding phase [6]. Since the use of precursors containing almost exclusively aluminosilicates
enables to form highly coordinated structure of the final product, the term “geopolymer” was introduced [7]. Good mechanical properties of alkali-activated/geopolymer cements and concretes have been proved in lots of structural applications around the world [8].

Geopolymers are usually manufactured from low-calcium source material, i.e. fly ash or metakaolin [9]. Metakaolin is produced by calcination of kaolinite clays at 500–900 °C. High reactivity of metakaolin particles in alkaline solution is achieved by optimal calcination temperature providing desired chemical and mineralogical composition. As long as costs of metakaolin production are higher in comparison to industrial by-products commonly used in alkali-activated binder technology, use of metakaolin geopolymers is predominantly studied in niche applications. Excellent fire resistance and durability in aggressive chemical environment [10] predetermine the use of metakaolin geopolymer in refractory applications or protective structures.

Carbon black, an amorphous form of elementary carbon, is produced by the incomplete combustion of hydrocarbon materials and used as a low-cost rubber reinforcing filler or black pigment. Colloidal carbon black particles exhibit high conductivity with chemical and thermal stability, therefore they can be successfully incorporated in conductive composites [11]. Mingqing et al. [12] used carbon black to manufacture cement mortar with enhanced conductivity that was laid as an indoor electrical heating slab. Lamuta et al. [13] studied metakaolin geopolymers and described the direct piezoelectric effect in their structure related to the migration of hydrated Na⁺ cations causing a charge imbalance and generation of local dipoles. Increased availability of mobile ions supplied by the alkaline activator thus causes lower electrical resistance of alkali-activated binders in comparison with cement-based materials [14]. Concerning the application of conductive admixtures in metakaolin geopolymers, MacKenzie et al. [15] states that the electrical conductivity of potassium-activated composites containing the same amounts of graphite was generally lower than those of the SWCNT containing samples.

2. Materials and methods

The main source materials for geopolymer matrix synthesis was metakaolin composed of almost exclusively aluminosilicates (chemical composition is given in Table 1) and water glass solution, commercially sold sodium silicate with molar ratio SiO₂/Na₂O = 1.6 (43 wt.% of dry mass). Conductive admixture - carbon black Vulcan 7H was added in dosage up to 4.0% of solid aluminosilicate precursor along with dispersing agent, 2% aqueous solution of non-ionic surfactant Triton X-100. Mortars were produced using standardized quartz sand as aggregate.

All mixtures were mixed according to proportions listed in Table 2 with water content adjusted to the same flow diameter on the flow table (EN 1015-3: 1999 [16]). Mixing procedure included following steps: first mixing the water glass with carbon black, dispersing agent and initial amount of water in laboratory mixer. After the homogenization, the quartz sand and remaining water were added. Right after mixing, geopolymer mortars were cast into prismatic 40 × 40 × 160 mm moulds, covered with a plastic sealant to protect the binder from moisture loss and left to set in laboratory conditions. After demoulding, the specimens were stored in laboratory till the age of impedance spectroscopy testing (40 days). Before the impedance spectroscopy, samples were dried (5 days at 105 °C) to reduce the influence of moisture on assessed electrical properties.

In order to perform the impedance spectroscopy, specimens were placed between parallel brass electrodes 30 × 100 mm (so that a distance between electrodes was 40 mm) and subjected to analysis in the range of 40 Hz to 1 MHz using an Agilent 33220A sinusoidal signal generator and an Agilent 54645A dual-channel oscilloscope. The output voltage of the signal generator was 5.5 V and the input values of the oscilloscope 13 pF and 1 MΩ for the electrical capacity and the resistance, respectively. These measurements were fully automated. At higher range of frequencies, 100 MHz up to 3 GHz, R&S ZNC vector analyzer with DAK 12 coaxial probe (Speag) has been used to measure the electrical conductivity and relative permittivity as a function of frequency. Seven days after the beginning of the electrical measurements, the specimens were tested for their mechanical properties (compressive and
flexural strength) and porosity by mercury intrusion porosimetry (Micromeritics Poresizer 9310). SEM images were taken using electron microscope Tescan MIRA3 XMU.

**Table 1.** Chemical composition of metakaolin.

|        | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | S_total | Na₂O | K₂O  |
|--------|------|-------|-------|------|------|---------|------|------|
| (%)    | 55.01| 40.94 | 0.55  | 0.55 | 0.14 | 0.34    | 0.09 | 0.06 |

**Table 2.** Mix composition of metakaolin geopolymer with carbon black.

|                  | REF  | CB-0.5 | CB-1  | CB-2  | CB-3  | CB-4  |
|------------------|------|--------|-------|-------|-------|-------|
| Metakaolin (g)   | 350  | 350    | 350   | 350   | 350   | 350   |
| Sodium silicate (g) | 350  | 350    | 350   | 350   | 350   | 350   |
| Carbon black (g) | -    | 1.75   | 3.5   | 7     | 10.5  | 14    |
| Aggregate (g)    | 1050 | 1050   | 1050  | 1050  | 1050  | 1400  |
| 2% Triton X-100 (ml) | -    | 2      | 3.5   | 7     | 10.5  | 14    |
| Water (g)        | 120  | 120    | 125   | 130   | 137   | 148   |

3. Results and discussion

3.1. Electrical properties

Electrical resistance depending on the carbon black concentration is depicted in Figure 1. At lower frequency range, the resistance decreased with higher amount of carbon black and with the frequency as well. The logarithmic scale was applied to distinguish a point of frequency around 50 kHz wherefrom the resistance of the reference material drops and remains the lowest among all samples while the specimens with carbon black exhibited similar behavior and minor differences in electrical resistance.

![Figure 1](image-url)
Electrical capacitance curves of samples with carbon black (Figure 2) showed an increment of capacitance, especially at low frequency. There was a steep decline of capacitance in the frequency spectrum up to 1 kHz. Samples CB-2 to CB-4 are close to each other and intersect several times across the spectrum. The reference frequency of 1 kHz was chosen to illustrate the changes of electrical properties, both resistance and capacitance values are shown in Table 3. Enhanced electrical capacitance and reduction of resistance with higher carbon black content is clear, with similar values of CB-2, CB-3 and CB-4.

**Figure 2.** Electrical capacitance of metakaolin geopolymer mortars with different carbon black content.

**Table 3.** Comparison of electrical resistance and capacitance at reference frequency 1 kHz.

|                | REF  | CB-0.5 | CB-1  | CB-2  | CB-3  | CB-4  |
|----------------|------|--------|-------|-------|-------|-------|
| Electrical capacitance (pF) | 3.71 | 8.97   | 14.95 | 24.28 | 28.99 | 22.83 |
| Electrical resistance (MW)      | 21.61| 8.87   | 5.13  | 3.30  | 2.75  | 3.51  |

Relative permittivity of the reference material without carbon black remains almost constant across the frequency spectrum, as can be seen from Figure 3. Relative permittivity of carbon black-doped material grew, with a slight decrease with frequency. This drop is more apparent with higher carbon black content and at the outset of the frequency applied. At 500 MHz, the relative permittivity increased from 2.8 to 5 in case of maximum carbon black concentration.
Figure 3. Relative permittivity of metakaolin geopolymer mortars with different carbon black content.

3.2. Mechanical performance
Compressive and flexural strength values of 47 days cured geopolymers are shown in Figure 4. Carbon black content of 0.5% was yet too low to worsen the mechanical properties but higher concentration from 1% caused a drop of strength, especially in compression. Sample CB-4 reached only 11.7 MPa, less than a half of the reference strength (27.5 MPa). Flexural strength was decreasing as well but it was less sensitive to the carbon black content.

Figure 4. Mechanical performance of metakaolin geopolymer mortars with different carbon black content.

3.3. Microstructure
Comparison of the cumulative intruded volume in Figure 5 shows that the presence of carbon black modified the pore structure of geopolymer matrix. With increasing carbon black content, the total pore volume rose from 0.14 to almost 0.19 cm³·g⁻¹ and higher number of pores of larger diameter occurred. Similarly, the SEM images in Figure 6 revealed that the microstructure of sample CB-4 (picture B) is porous and clearly less compact compared to the reference sample (picture A). Picture C depicts the agglomerates of carbon black we traced among the binding phase and other products. Bright platelet formations are probably crystals of sodium carbonate crystals found in CB-4 matrix only. The results of porosimetry and electron microscopy correspond well with mechanical strength values achieved.

Figure 5. Cumulative intruded volume of metakaolin geopolymer mortars with different carbon black content.

Figure 6. SEM images of metakaolin geopolymer mortars with different carbon black content.
4. Conclusions
Alkali-activated binders have been reported to possess potential in fabrication of smart conductive composites. Metakaolin geopolymeric mortars were chosen to investigate the contribution of carbon black (up to 4%) to the enhancement of their electrical properties tested using impedance spectroscopy analysis. Carbon black content from 1% led to drop in electrical resistance across the frequency spectrum up to 50 kHz while the improvement of electrical capacitance was obvious throughout the whole measurement frequency range. The electrical capacitance and resistance of samples with 2, 3 and 4% of carbon black were similar, only the relative permittivity (measured at higher frequency) increased with each carbon black addition. From the results of mechanical performance and microstructural observation it seems that the increase of carbon black concentration from 2 to 4% does not have a considerable effect on the principal electrical parameters but deteriorates the binder quality. Drop of compressive strength is probably associated with multiple factors. Incorporation of nanosized carbon black particles involves additional requirements for wetting and results in increase of pore volume. Moreover, extremely small dimensions of the functional filler make the filler-matrix interface area enormous and poor binding of the matrix to the filler greatly affects the conductivity potential and mechanical performance as well.

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