Silicate conductive composites with graphite-based fillers

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Abstract. Electroconductive composites are modern materials that are commonly used in many industries such as construction industry and machine-building industry. For example, these materials can be useful as sensors for monitoring changes in constructions, shielding stray currents from electrification networks, shielding electromagnetic radiation in operating rooms, cathodic protection against moisture or overvoltage protection of buildings. The topic of this post is the research of electrically conductive silicate composites with graphite-based fillers. In this research will be tested composites with different ratio and types of graphite and monitor their electroconductive properties like impedance, and physical-mechanical properties like compressive and tensile strength. The post describes basic properties and interactions of silicate electrically conductive composites with graphite fillers. It was found that by adding 10 % wt. graphite into silicate composites, impedance is reduced by 50% and compressive strength by 40%. The flexural tensile strength depends mainly on the roughness of the particles, where the coarser flaky particles transfer the load better and increase the strength while very fine graphites reduce the flexural tensile strength. Furthermore, it has been found that very finely ground synthetic graphites are most suitable for achieving low impedance of composites.

1. Introduction

Composite materials create a wide range of options that can be used to make a variety of materials designed specifically to current market requirements, research, and development. The composites are consisting of two or more substances with different chemical components that differ in physical and mechanical properties.

In most cases, one or more substances form a so-called filler, which represents a discontinuous phase in composite materials. By mixing fillers into the matrix, many physical, chemical, and mechanical properties of the composite material can be modified, such as bulk density, compressive strength, tensile strength, bulk stability, thermal and electrical conductivity, vapor and gas permeability, absorbency, and many other characteristics. Another benefit of fillers can be a reduction in production costs.

Another component of composites is a matrix, which has the main task of bonding all components into one integral material, forming a continuous phase of the material, and acting as a binder. Its function is also to maintain the desired shape and affects the final appearance of the material. The matrix contributes to the mechanical and physical properties of the entire composite material. It also has the task of protecting the fillers or reinforcement from external influences, determines the thermal conductivity, fire resistance of the composite and others. Matrices are most often based on silicate materials such as cement, based on polymer, such as epoxies and polyesters, or based on geopolymer.

Electroconductive composites can be defined as composites with a certain filler content that provide suitable electroconductive properties. With the help of electrically conductive fillers, a stable, perfectly electrically conductive network is created in the material, which can conduct electric current. For solid materials, the electrical conductivity can be divided into surface and internal conductivity. Surface electrical conductivity depends mainly on the moisture of the material, while internal conductivity is related to the structure, amount and properties of conductive fillers used [1].

As electrically conductive fillers, carbon-based fillers such as carbon black, graphite, carbon, carbon nanoplates or graphene, carbon nanotubes, carbon tubes, micro-silica and others are most commonly used, and metal-based fillers such as however, steel wires, fabrics, or powders for these fillers are less effective and are not suitable for silicate composites [1][2][3].

Impedance, analogous to specific electrical resistance (resistivity) is a property of a material when a direct current passes through it, impedance is a "resistance" for alternating current. It is a complex quantity that consists of an imaginary and a real component. For accurate measurement, it is necessary to precisely define the measured quantities (voltage and current).

Once there is a whole, perfectly interconnected electrically conductive structure in the composite material, the impedance of the material itself decreases significantly, this limit is called the percolation threshold and results in the subsequent addition of the material no longer affecting the impedance of the composite [3][4][4].

The properties of silicate composites significantly depending on the type and amount of filler used. With the addition of carbon-based fillers, there is a significant decrease in physical and mechanical properties but also a significant reduction in impedance. These properties are interrelated and depend on the amount of filler. By comparing the different amounts of different types of electrically conductive fillers and their influence on the physically mechanical and electrically conductive properties, no one has study it so far and it is a relatively neglected topic.

In construction, these materials are becoming key elements for monitoring the degradation of building structures, shielding stray currents from electrification networks, shielding electromagnetic radiation in hospital rooms, cathodic protection against moisture, overvoltage protection of buildings, resistance-heated concrete or signal shielding for prison facilities [1].

2. Materials

To verify the effect of the amount of graphite on the electrically conductive and mechanical properties of the composite were designed composites consisting only of cement and graphite were created to eliminate the negative effects of any electrically non-conductive fillers used. Four types of industrially produced graphite were used as conductive filler, representing natural and synthetic graphites, coarse and fine fractions and one with improved electroconductive properties by surface treatment (graphite C). The most important parameters of the graphites used are listed in Table 1.

Table 1. Properties of used electrically conductive fillers.

Graphite	Genesis	Particle type	Specific surface [m²/Kg]	Impedance [Ω]
A	Natural	Flat flakes	1087	0.98
B	Natural	Irregular flakes	12187	1,45
C	Natural	Irregular with adjustment	19879	0.93
D	Synthetic	Irregular	12499	1.19

Portland cement CEM I 42.5 R according to EN 197-1 was used as a binder for the silicate composite. It is a commonly used cement with a designation with a faster increase in strength than ordinary cement of a similar class. The basic properties of CEM I 42.5 R cement according to the manufacturer are summarized in Table 2.

Table 2. Properties of cement.

Type	Density [kg/m^2]	Specific surface [m²/kg]	Impedance [Ω]
Cement CEM I 42,5 R	3110	391	$7.66 \cdot 10^6$

Graphite was dosed into the composite by weight, in proportions of 4,7,10 and 13% by weight of cement. These values were chosen deliberately on the basis of experience from professional publications [1], where they state that the percolation threshold of graphites is about 10% by weight. Consequently, higher doses of graphite than the percolation threshold would not be effective. Cement and water were also dosed by weight. The water coefficient wc = 0.35 was used. The composition of the mixtures is given in the following table. The properties were verified for each type and dose of graphite on 9 test samples, in total the properties were verified on 144 samples.

Table 3. Composition of the mixture.

Designation of the mixture	Cement (%)	Graphite (A, B, C, D %)
A 4	96	4
A 7	93	7
A 10	90	10
A 13	87	13
B 4	96	4
B 7	93	7
B 10	90	10
B 13	87	13
C 4	96	4
C 7	93	7
C 10	90	10
C 13	87	13
D 4	96	4
D 7	93	7
D 10	90	10
D 13	87	13

3. Methods

Important parameters were determined on all input raw materials, which were the impedance determining the conductivity of the raw materials and the specific surface area, which indicates the grain size and character of the particles. Furthermore, the shape of the grains was specified using an electron microscope.

The specific surface area of the electrically conductive fillers and cements used was determined using BET methods according to ISO 9277: 1995 (E) [6].

The impedance of raw materials and formed composites was determined using a GW Instek LCR-6020 measuring device at a voltage of 1.0 kHz. The impedance of the raw materials like graphite and cement was measured using a mould with electrodes printed on a 3D printer, which is shown in Figure 1. The impedance of the composites was determined on samples of 40x40x160 mm, which is shown in Figure 2, in which copper electrodes are built in. Figure 3 at a distance of 120 mm. The course of measuring the impedance of composites is shown in Figure 4. Impedance measurementFigure 4 the device is connected directly to the electrodes of the composite.

Figure 1. Measuring device GW Instek LCR-6020.

Figure 2. Composite test specimen for impedance measurement.

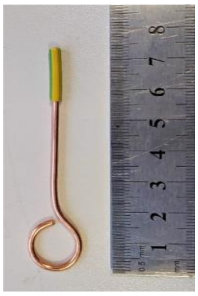

Figure 3. Electrode.

Figure 4. Impedance measurement.

The physical and mechanical properties of the composites were determined after 28 days of maturation in a standard environment on test specimens 40x40x160 mm. The flexural tensile strength was determined on the samples using three-point bending, according to ČSN EN 12390-5. Compressive tensile strength was determined on fractions of samples from the determination of flexural tensile strength in accordance with ČSN EN 12390-3 [7].

4. Results

The results of impedance measurements and determination of compressive strength and flexural tensile strength after 28 days for composites with different amounts and types of graphite are evaluated in Figure 5, Figure 6 and Figure 7.

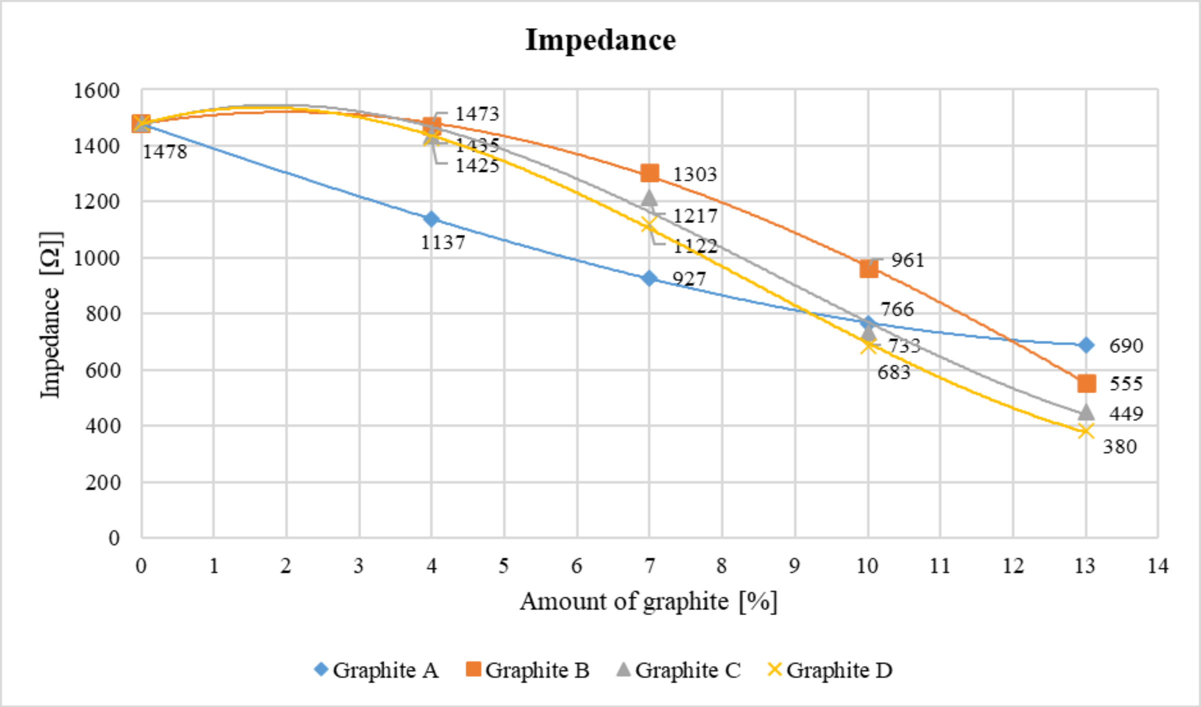

Figure 5. Influence of graphite amount on impedance of composite.

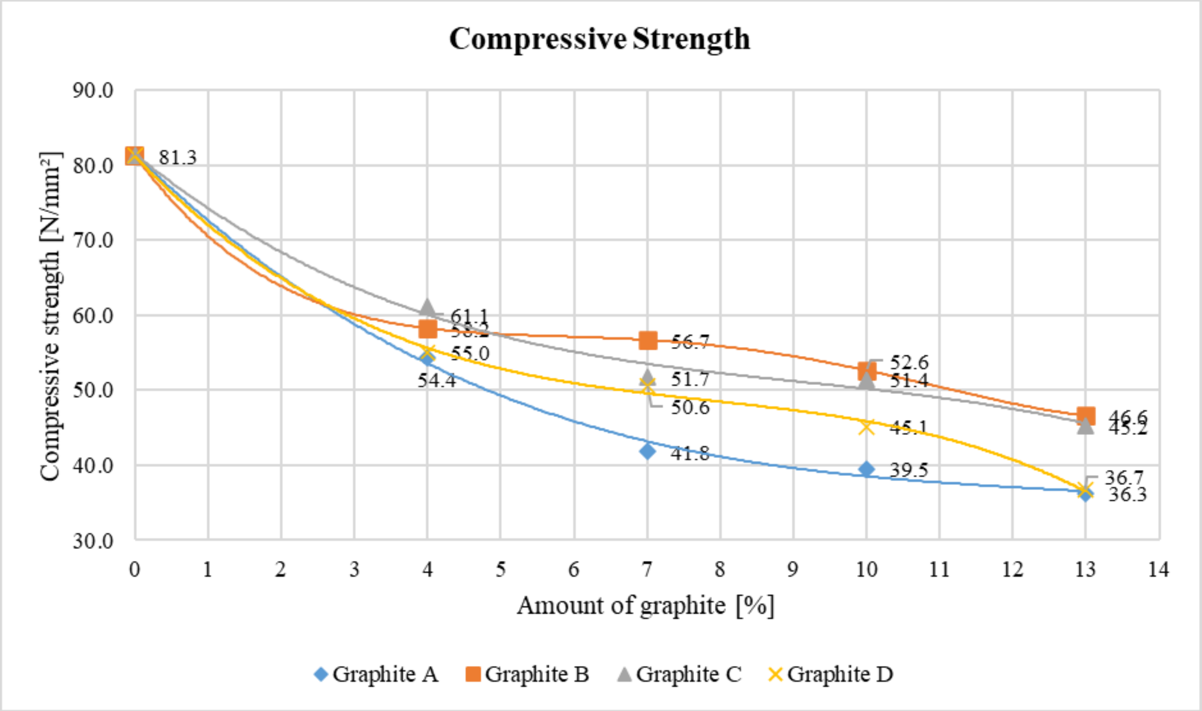

Figure 6. Influence of graphite amount on compressive strength of composites.

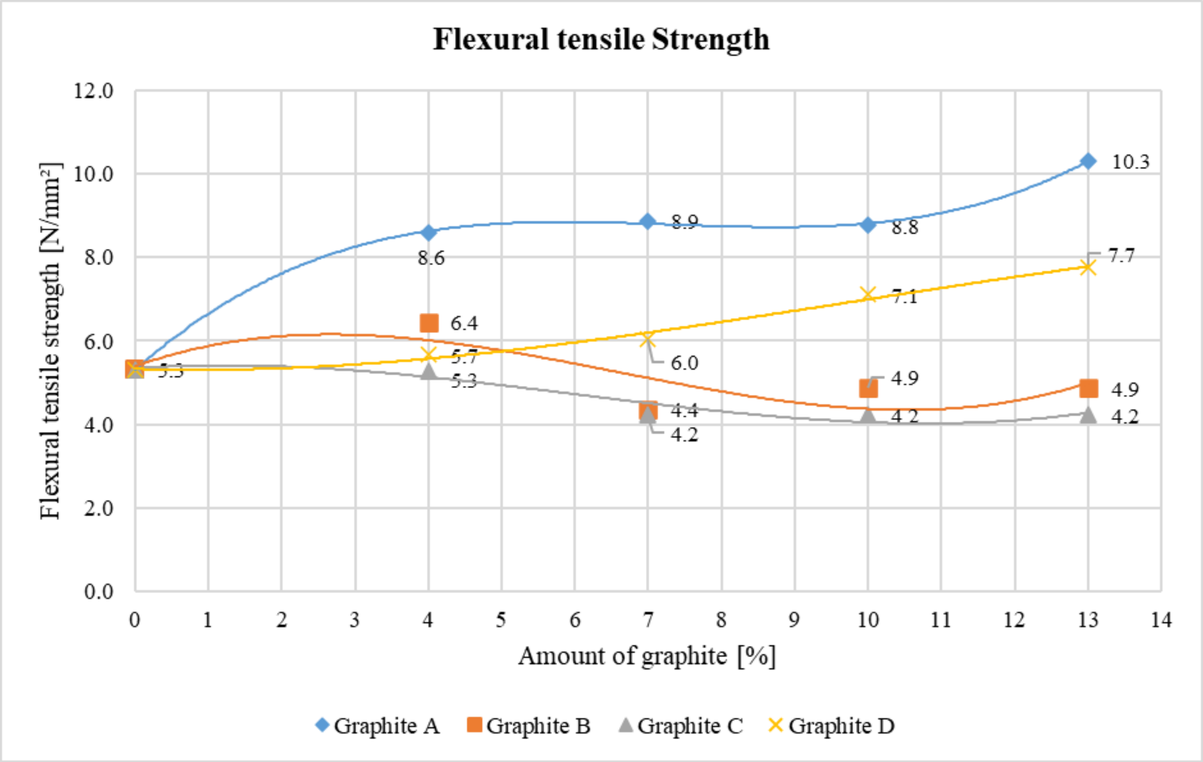

Figure 7. Influence of the amount of graphite on the tensile strength in bending of composites.

With the addition of graphite to the composite, its impedance decreases significantly. The highest decrease was recorded at a dose of 13% by weight, but according to the trend, the percolation threshold, which is given around 10% by weight, probably did not be reached. Impedance was reduced at doses of 4/7/10 and 13% by an average of 8/22/47 and 65%.

The physical and mechanical properties are also affected by the addition of graphite to the composition, the flexural tensile strength has been improved using coarse graphite type (graphite A) and (graphite D) with medium grain size and irregular volume type, this improvement being relatively affected by compaction. In the case of compressive strength, a significant decrease was recorded already with the addition of 4% graphite, when the strength in the first decreased by 30%. At a dose of 7% the compressive strength decreased by 38%, at 10% graphite the strength decreased by 42% and at a dose of 13% graphite the compressive strength decreased by 50%.

From the above results, with the addition of graphite to composite, mainly affects the impedance and compressive strength of the composite, these values decrease from a long-term point in proportion to the increasing dose of filler.

5. Conclusion

The aim of this paper was to monitor the electroconductive and physical-mechanical properties and their interactions in silicate composites with a carbon-based filler. Various doses and types of graphite were tested and at the same time the impedance, compressive strength and flexural tensile strength of composites were monitored.

By introducing suitable types of graphite into the silicate composite, its electrically conductive, physical, and mechanical properties can be significantly influenced. Graphite as a filler is an effective material to reduce impedance. At a dose of 10% graphite the impedance is reduced by 50%, with the compressive strength decreasing by about 40%. The values of these properties decrease symmetrically according to trends with each added percentage of filler. The flexural tensile strength is mainly affected by the grain size of the filler, with coarser types of flake-type graphite having a higher ability to transmit forces in the material, while fine graphite types reduce the flexural tensile strength.

Synthetic graphite and graphites with irregular and very fine particles have been shown to be more effective in achieving lower impedance values. This is due to the larger specific surface area of the particles, and thus the higher probability of contact of irregular grain surfaces in the composite matrix. The different impedance of the graphites themselves as the raw material does not affect the impedance of the entire composite. It can be said that the impedance of the composite depends mainly on the suitability of the size, shape of the particles and the effective amount of the conductive filler used in composite.

6. References

[1] Wu J, Liu J and Yang F 2015 Three-phase composite conductive concrete for pavement deicing *Construction and Building Materials* **75** 129–135 (Amsterdam: North-Holland/American Elsevier)

[2] Terashita K, Tanaka T, Nishimura K and Miyanami K 1993 Continuous kneading for electrically conductive composite materials and evaluation of filler dispersion state *Bulletin of the University of Osaka Prefecture, Series (An Engineering and Natural Sciences* vol 421) pp 51–67

[3] Rhee I, Lee J S, Kim Y A, Kim J H and Kim J H 2016 Electrically conductive cement mortar: Incorporating rice husk-derived high-surface-area graphene: Incorporating rice husk-derived high-surface-area graphene *Construction and Building Materials* **125** 632–42

[4] Xie P, Gu Ping and Beaudoin J J 1996 Electrical percolation phenomena in cement composites containing conductive fibres *Journal of Materials Science* **31** 15 4093–97

[5] Kim G M, Park S M, Ryu G U and Lee H K 2017 Electrical characteristics of hierarchical conductive pathways in cementitious composites incorporating CNT and carbon fiber *Concrete Composites* **82** 165–75

[6] ISO 9277:1995(E) *Determination of the specific surface area of solids by gas adsorption using the BET method*

[7] ČSN EN 12390-5 2020 *Testing hardened concrete – Part 5: Flexural strength of test specimens*

[8] ČSN EN 12390-3 2019 *Testing hardened concrete - Part 3: Compressive strength of test specimens*

Acknowledgments

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