Development of conductive composite coatings with specific functional properties

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Abstract. The article presents the development results of advanced composite coatings with enhanced electric conductivity intended for detection of disruptions in the base material structure. Conductive coatings were prepared from a low viscosity epoxy resin and three types of admixtures - amorphous carbon black, micronized graphite and multi-walled carbon nanotubes (MWCNTs). Such multicomponent coatings were tested together with hand-applied graphite layers and commercial spray-applied colloidal graphite and copper-based electroconductive coatings, for comparison. The influence of the admixtures on electrical conductivity was evaluated. The course of impedance response of polymer coatings, graphite layers and copper layers was investigated during bending in press, drilling and high-speed loading by rifle projectiles. Conductive coatings showed a distinctive change in impedance under mechanical damaging by drilling and during dynamic testing. These functional coatings represent innovative direction for the development of new progressive ballistic and anti-blast shield systems.

1. Introduction
The number of terrorist attacks and their victims is growing dramatically in the world. Ensuring security of the population and protecting critical infrastructure against terrorist threats is one of the key challenges of current era. One of the protection options are progressive mobile barrier systems that are resistant to dynamic threats (projectiles, explosions). These are, for example, ballistic and counter-explosive shield systems with damage detection function. The aim of presented research is to develop a segment of ballistic and anti-blast shield systems, which, in conjunction with the monitoring system, will detect damage in the structural integrity of the material.

In previous research [1–8], it was found that conductive concrete with an appropriate dosage of electrically conductive particles and/or fibers exhibit the properties necessary for strain monitoring and detecting its own material structure damage during both static and dynamic loading. However, the complexity of the cement composites behavior and above all, difficult reproducibility of the results in changing climatic conditions quite complicates their possible use. Therefore, easy-to-apply thin-film coating sensors were investigated to offset the disadvantages of the cementitious composites.

Generally, conductive coatings contain conductive components such as carbon black, metallic components (copper, silver) or carbon nanoparticles. Several articles comparing these functional fillers have been published recently. Berkei et al. [9] investigated the electrical properties and percolation threshold of carbon nanotubes. Low concentrations from 0.5% to 1% phr (parts per hundred rubber) carbon nanotubes result in anti-static properties, whereas electrical conductivity is reached in the range of 2–4% phr. In contrast, in some coatings even high concentrations of 8% phr carbon nanotubes show
no effect at all. Tinthoff et al. [10] have confirmed in their research that MWCNTs can be used as an alternative to the classical conductive pigments like carbon black or metallic particles. Senesac and Thundat [11] investigated the piezoresistive properties of experimental nano-cantilever beam sensors. Single-walled carbon nanotubes (SWCNTs) could be used for explosion detection.

2. Materials and methods

2.1. Technology of preparation and application of coatings

The increased electrical conductivity of the coatings was achieved by the appropriate choice of matrix, functional micro/nano admixtures, their optimum amount and also the preparation technology itself. Initially, 25 samples of conductive coatings with varied composition were prepared from a low viscosity epoxy resin and styrene-butadiene dispersion with following fillers incorporated (see Figures 1a-c):

- amorphous carbon black (up to 6% w/w),
- micronized graphite (up to 20% w/w),
- multi-walled carbon nanotubes (MWCNTs, 0.5% w/w).

To reduce system viscosity and ease the application, volatile substances (acetone, technical alcohol and gasoline, isopropyl alcohol, etc.) were added into the mixture. Components were stirred by Silverson LSM-A high shear laboratory mixer at 5000 rpm for 5 minutes. This procedure provided a high degree of mixture dispersion but only for epoxy resin samples. Unfortunately, styrene-butadiene polymer samples could not be adequately mixed with functional fillers so the workability was considerably worse, thus only a limited number of testing bodies was prepared. All prepared materials were consecutively applied onto the surface of glass fiber reinforced concrete (GFRC) with a plastic spatula, a brush or a roller. All these ways created a thin film.

The mentioned coatings were supplemented with hand-applied graphite lead layers and commercially available spray-applied electroconductive lacquers based on colloidal graphite and copper, see Figure 2. All these coatings were also applied on the surface of GFRC.

2.2. Dispersion analysis of conductive components in coatings

In the first phase of testing, the dispersion of conductive components in individual matrices was investigated. Microscopic analysis and visual assessment of the mirror gloss of the surface were performed on the hardened epoxy coatings, see Figures 3a-c. The next step was to verify the degree of electrical conductivity and its uniformity over the entire surface of the coating, see Figure 4.

Alternating current was used to measure the electrical properties of conductive coatings. The resistance to this alternating current is expressed by the electrical impedance in ohms Ω and measured by a hand-held LCR meter (and impedance analyzer-recorder) by a direct two-point method at the corners of the test specimens during positive half-waves of excited alternating current with a frequency of 1 kHz at voltage of 1 V. The impedance of the composite coating depends on the distance between copper electrodes. The length of the element (l) is directly proportional to impedance.
In contrast, the impedance is in inverse proportion to the active surface (S):

\[ R = \frac{r \times l}{S} \]  

where \( r \) is specific impedance of the material and \( R \) is impedance of the element.

![Figure 3. Microscopic analysis of the conductive coatings: (a) matt surface; (b) glossy surface; (c) matt/gloss transition; (d) wrinkle structure of MWCNTs-enriched coating.](image)

![Figure 4. The measurement of impedance.](image)

2.3. Impedance response testing under mechanical damage

Impedance measurements of the conductive coatings under mechanical stress was performed by a test ripping machine TIRA test 2710. Contact parts of the press were separated by electrical insulation. Individual samples of conductive polymer coatings on GFRC boards (250 × 250 × 10 mm), and graphite and copper layers on GFRC boards (250 × 50 × 10 mm) were statically loaded with a three-point bend. The coatings were directly connected to a digital impedance measurement device by clamped contacts.

Promising samples were subsequently damaged by hand drilling device. The hole was drilled through GFRC base boards and the drill penetrated the conductive coating on the other side. The conductive coatings were directly connected to the impedance meter via clamped contacts.

2.4. The testing of impedance response during ballistic loading

Three types of promising conductive coatings were prepared for dynamic testing, which were applied onto dried and cleaned GFRC surfaces with glued copper contacts (i.e. grounding tape). The coatings were: epoxy coating with amorphous carbon black incorporated (6% w/w), surface-applied graphite lead and spray-applied electroconductive graphite lacquer. The contact parts of the coatings were provided with an electrically insulating tape after curing, see Figures 5a-c. For comparison, a second series of identical coatings were provided with self-adhesive conductive tape (instead of glued tape) and covered with a transparent non-conductive epoxy gel, protecting against mechanical damage, humidity and weather, see Figures 5d-f.

![Figure 5. (a) Epoxy resin/carbon black coating; (b) graphite coating, (c) graphite lacquer; Epoxy-gel encapsulated samples of: (d) epoxy resin/carbon black coating; (e) graphite coating; (f) graphite lacquer.](image)
Both nondestructive and destructive tests were carried out in a ballistic laboratory test tunnel. The impedance of the conductive coatings was measured during a perpendicular impact of the 7.62 × 51 mm NATO ball ammunition. The main measuring device was an impedance analyzer with a recording computer. The test specimens were connected to the apparatus via a two-conductor copper wire and crocodile clips. The test samples were loaded with rifle projectiles with initial velocity of 830 m·s⁻¹. Individual shots were aimed at a minimum pitch of 12 cm, see Figure 6.

Non-destructive testing was ensured by ballistically-resistant cover plates made of densely steel fiber reinforced concrete (SFRC). During destructive experiments, the samples were only covered with GFRC, see Figures 7–8. Each sample was subjected to four shots, two non-destructive and two destructive.

3. Results and discussion

3.1. Preparation technology and application methods
In the first phase of the tests, the preparation technology and the application method for coatings with functional micro/nano admixtures incorporated was verified. Based on evaluation of application and functional properties, a selection of suitable binders and additives was conducted. Doses of the active ingredients, the time of homogenization and the mode of application were optimized. The dispersion of functional fillers has considerable effect on the final properties of the epoxy coating. Carbon epoxides need to be applied in one very thin film layer (e.g. with a roller) onto adsorbent substrates to spread the coating uniformly and without creating non-conductive resin layers. Insufficient dispersion of the filler in the surface layer is visible to the naked eye. Microscopic coating analyses corresponded with the results of gloss intensity evaluation. Epoxy coatings with evenly dispersed carbon filler (with low and stable impedance) show lower values of mirror gloss.

3.2. Impedance measurements of non-loaded samples
In the second phase of the project, samples with the most beneficial properties, i.e. the lowest impedance, were identified. Among the low-viscosity epoxy resins, the sample enriched with amorphous carbon
black (3% w/w) achieved stable impedance below 5 kΩ. MWCNTs-doped samples were less applicable as they exhibited tendency to create wrinkled structure (see Figure 3d) and showed a little higher impedance, about 12 kΩ. Micronized graphite, unlike nanotubes, was easily dosed in large quantities up to 20% w/w. However, nor better neither more stable coating impedance (50–100 kΩ) was achieved with such high dosage.

The styrene-butadiene matrix dispersions were less workable and did not create conducting chains, i.e. showed extremely high impedance, almost beyond measurability.

The most satisfactory results of impedance measurements were achieved with:

- epoxy coatings enriched with conductive carbon black (3% w/w),
- surface-applied graphite lead layer,
- electroconductive lacquer based on colloidal graphite.

These three samples also exhibited the best results under static and dynamic load, as shown in 3.3.

3.3. Impedance measurements of statically and dynamically loaded samples

The most promising samples after impedance measurements with no load were subjected to impedance measurements during static loading, i.e. bending. Almost none of the conductive coatings transforms the bending load into an evaluable impedance change. The only exception was the hand-applied graphite. During the bending test, the impedance began to increase after reaching 2/3 of the maximum applied force. In a drilling test, three variants of conductive coatings exhibited a measurable increase in impedance (see Figure 9) and were subjected to dynamic loading tests.

![Figure 9](image-url)

**Figure 9.** Course of impedance under mechanical damage by drilling (a) carbon black coating; (b) graphite coating; (c) graphite lacquer.

During dynamic processes, all three tested materials exhibited a significant change of impedance. The individual impacts of projectiles were well recognizable in impedance course graphs. The impedance of the samples increased during both destructive and non-destructive testing methods, see Figure 10.
4. Conclusion
The thin-film sensor coatings with enhanced electric conductivity represent an innovative direction for the development of ‘smart’ blast-resistant and ballistic-resistant barriers with failure detection ability. Easy-to-apply conductive coatings can be prepared from low viscosity epoxy resin with amorphous carbon black incorporated. Similar results were achieved using surface-applied graphite lead and spray-applied electroconductive graphite lacquer. Sensor coatings with non-conductive epoxy gel encapsulation (protecting against mechanical damage, humidity and weather) showed similar detection properties to the identical coatings without encapsulation. The conductive epoxy coating and graphite layers enable detection of material structure damage under dynamic ballistic loading. The materials exhibited impedance change both during direct damage of the matrix, and after indirect impact through a cover plate. Before practical use of these sensor coatings, verification of the results reproducibility in changing climatic conditions is advised.

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Figure 10. Course of impedance under ballistic loading (a) carbon black coating; (b) graphite coating; (c) graphite lacquer.
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