

Plasma-Modified N-Doped Graphene for Self-Sensing Cementitious Composites with Refinery Waste

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Introduction

The development of multifunctional structural materials combining mechanical performance with enhanced electrical properties is an important research direction in modern materials engineering. This study investigates cementitious composites modified with graphene-based paste and spent FCC catalyst from petroleum refining processes, combining nanomaterial functionalization with industrial waste utilization. Graphene-based paste was introduced as a conductive additive to improve the electrical properties of the cementitious matrix. In order to enhance its performance, the paste was subjected to dielectric barrier discharge plasma treatment. The use of DBD modification was intended to improve the functional behavior of the graphene-based additive in cementitious composites. The spent FCC catalyst was used as a mineral additive and partial cement substitute, contributing to the development of more sustainable cement-based materials. The experimental program included cementitious mixtures with varying graphene contents and a constant amount of FCC catalyst. The investigation focused on the electrical properties of graphene suspensions, fresh mixtures and hardened composites, as well as selected early-age mechanical properties. The results indicate improved electrical conductivity while maintaining satisfactory mechanical performance. The developed composites may provide a basis for further research on smart cement-based materials for structural monitoring applications.

Materials

The cementitious composite was prepared using the following materials: limestone Portland cement EN 197-1, class 42.5 R, supplied by Cementownia Ożarów (CEM II/A-LL); quartz sand with a particle size of up to 1.4 mm; Sika® ViscoCrete®-3225 EPL superplasticizer supplied by Sika; graphene paste in the form of an ultrasonically prepared aqueous dispersion; spent catalyst from the fluid catalytic cracking process (ECAT); and tap water.

In order to ensure uniform distribution of the graphene paste within the composite, an ultrasonic aqueous graphene dispersion was prepared. This allowed the graphene to be introduced into the mixing water in the form of a stable suspension. For this purpose, 30 g of graphene paste was added to 1 L of water and sonicated for 30 min until a homogeneous suspension was obtained. The dispersion of graphene paste in water was prepared using a UP400St ultrasonic homogenizer manufactured by Hielscher. The same preparation procedure was applied for both unmodified graphene and DBD-modified graphene.

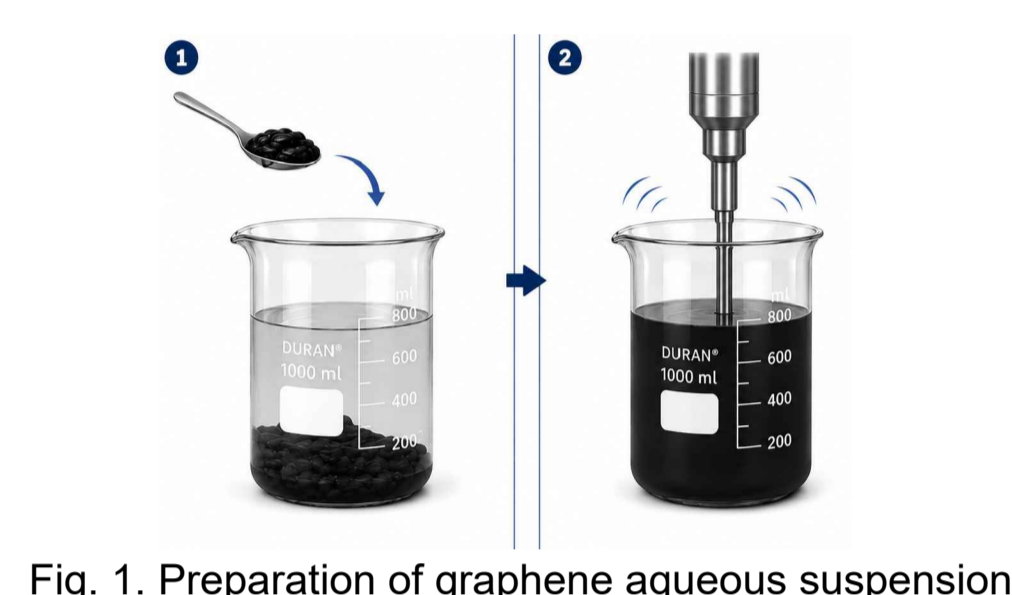


Fig. 1. Preparation of graphene aqueous suspension

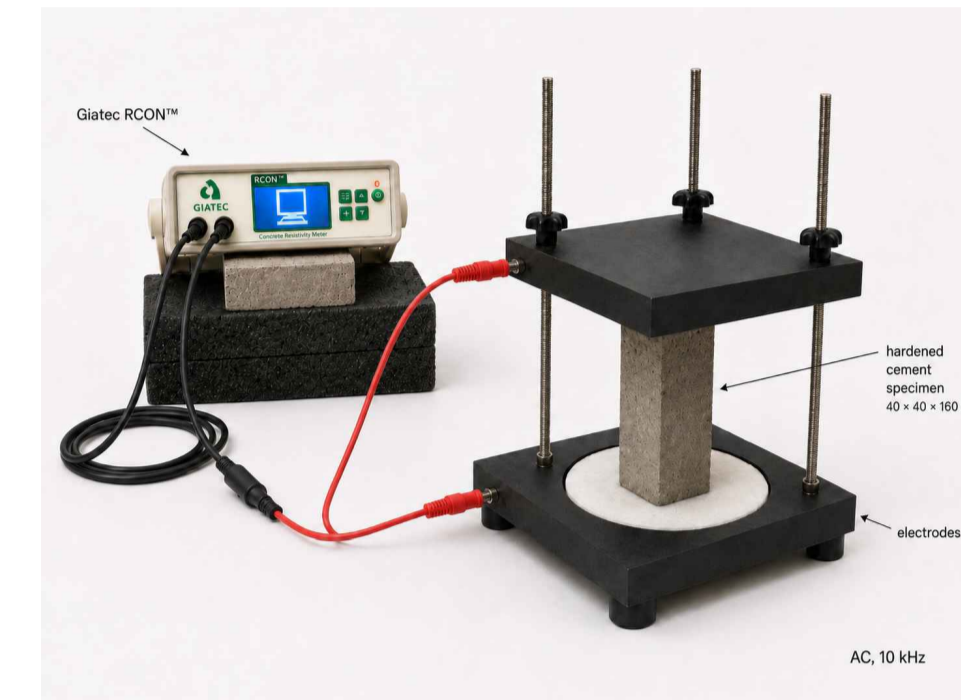


Fig. 7. Hardened sample resistivity measurement



Fig. 8. ZD-40 hydraulic testing machine

After 7 days of curing, flexural and compressive strength were also determined using a ZD-40 hydraulic testing machine. The obtained results made it possible to evaluate the relationship between the electrical and mechanical properties of cementitious composites modified with graphene and ECAT.

Graphene modification using DBD plasma

The graphene paste was subjected to plasma treatment using a dielectric barrier discharge (DBD) system. The process was carried out using a CTP-2000K plasma generator under ambient air conditions for 2.5 min.

The process parameters included a voltage of 100 V and a current of 0.95 A. The graphene paste was evenly distributed in a quartz chamber to ensure the most uniform possible exposure to plasma.

DBD treatment was applied to modify the surface properties of graphene and improve its functional behavior in a water-cement environment.

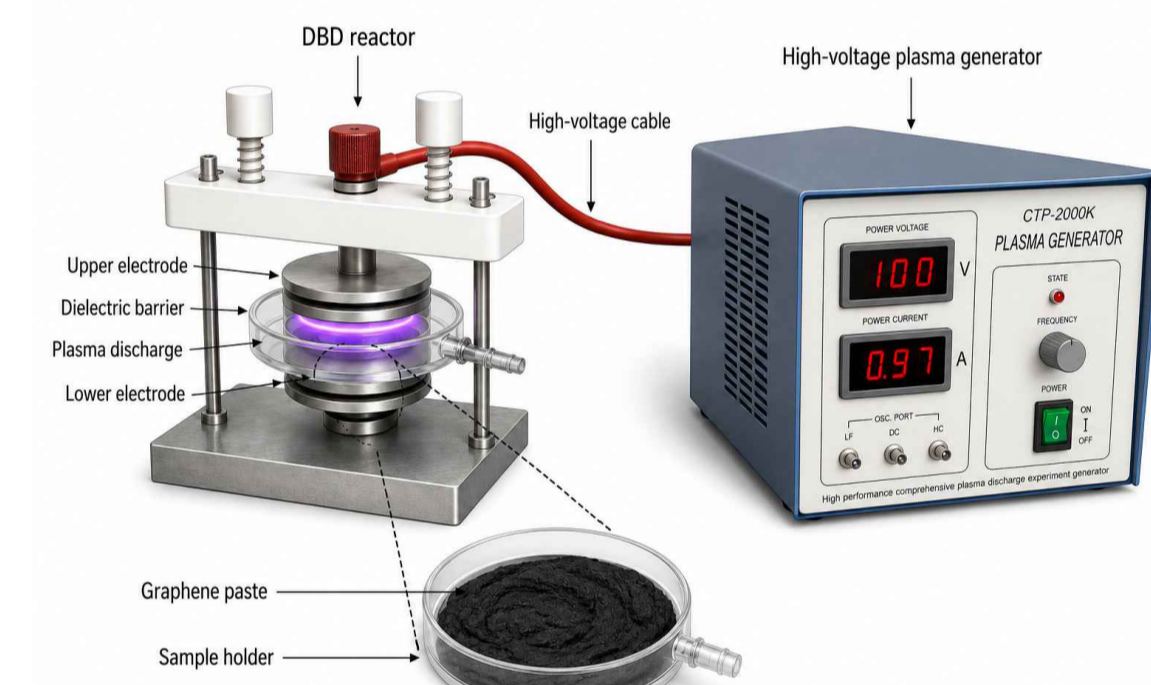


Fig. 2. Scheme of the DBD plasma treatment setup

Preparation of cementitious mixtures

The cementitious composite samples were prepared with varying contents of graphene aqueous dispersion and a constant amount of ECAT. Seven cementitious mixture formulations were developed. All mixtures were prepared using a laboratory mixer according to a specially developed procedure aimed at obtaining a self-compacting mixture.



Fig. 3. Scheme of cementitious sample preparation

Experimental Testing Program

To assess the influence of graphene plasma modification and the addition of ECAT, electrical and mechanical properties were investigated at different stages of composite development. In the first stage, the electrical conductivity and pH of graphene paste suspensions were determined by comparing unmodified paste with DBD plasma-modified paste. Subsequently, impedance measurements were performed using a Giatec RCON™ device, and the electrical resistivity of graphene pastes, fresh cementitious mixtures, and hardened samples was determined.



Fig. 4. pH and EC measurement

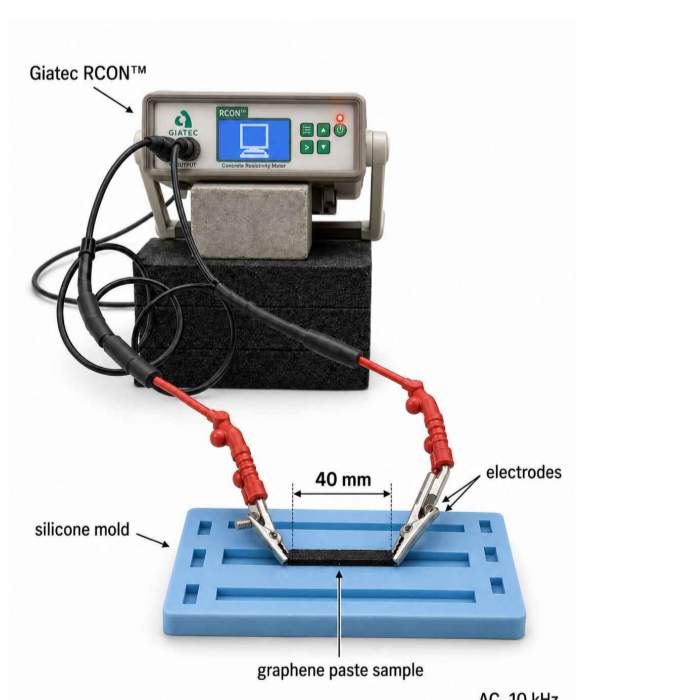


Fig. 5. Graphene paste resistivity measurement

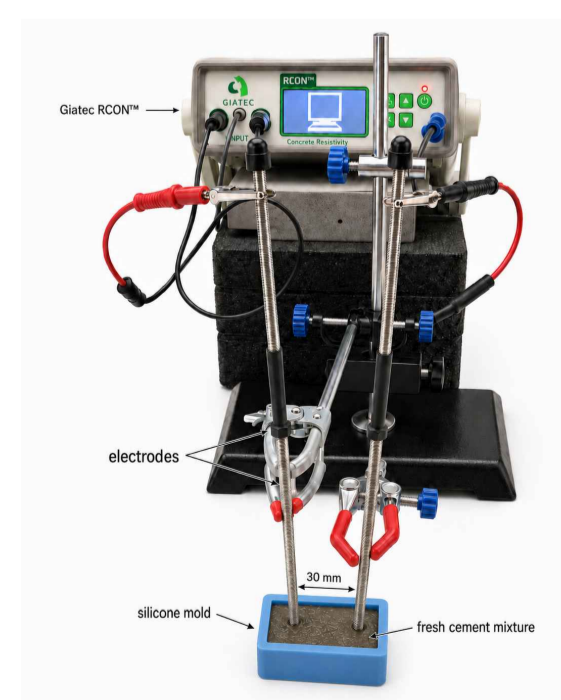


Fig. 6. Fresh mixture resistivity measurement

The measurements were carried out using alternating current (AC) at a frequency of 10 kHz, with values recorded at 5 s intervals. The electrical resistivity of hardened composites was determined after 2, 3, and 7 days of curing. Additionally, the samples tested after 3 days were dried for 24 h at 25°C to assess the influence of moisture content on the electrical properties of the material.

Results

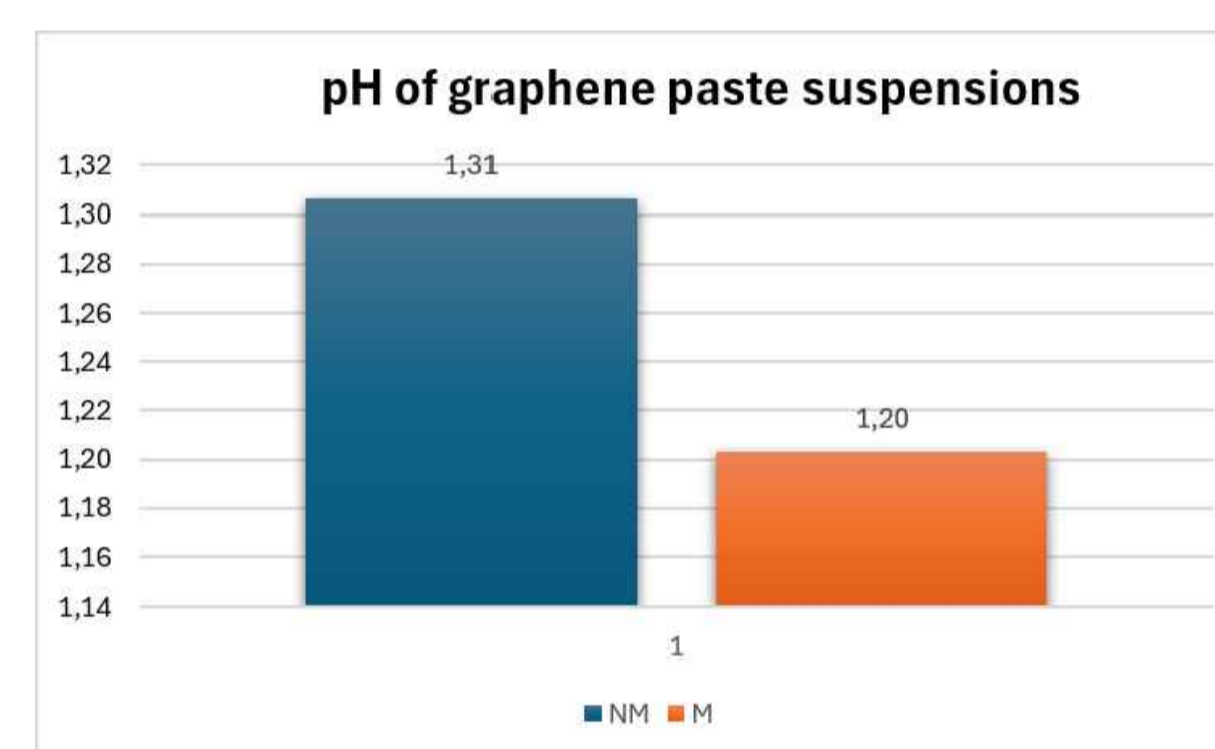


Fig. 9. pH values of unmodified and DBD-modified graphene paste suspensions.

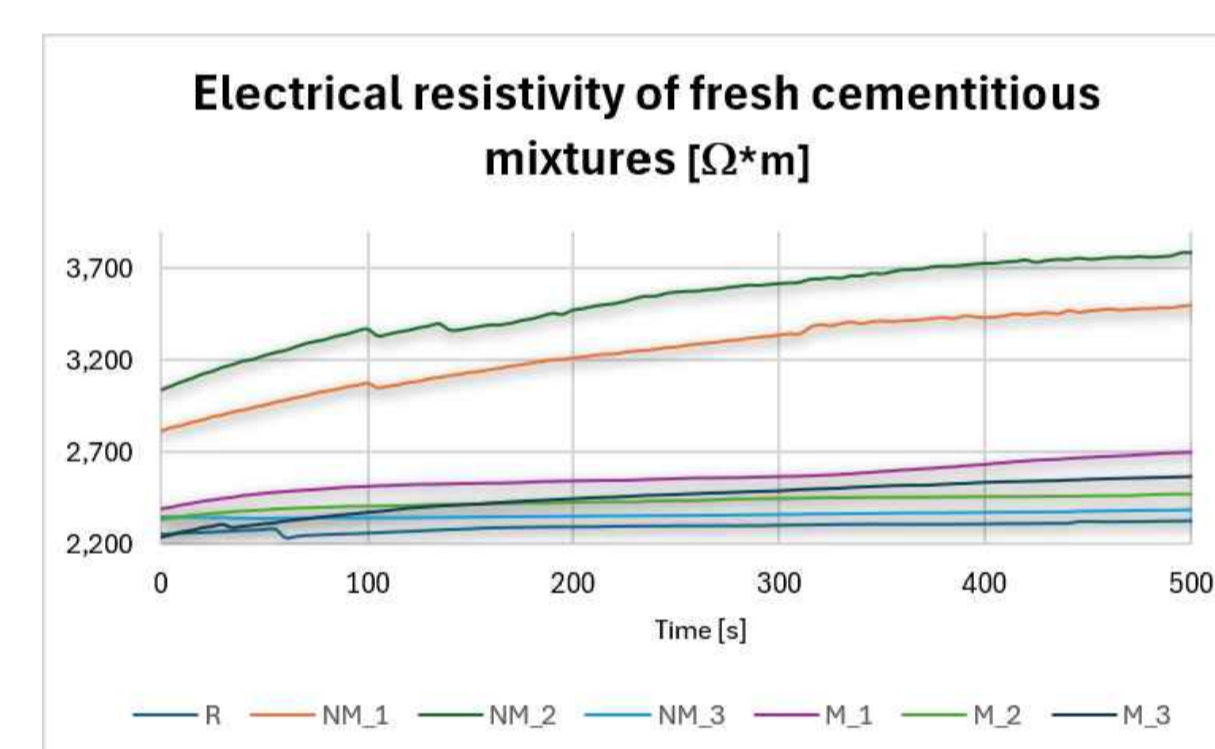
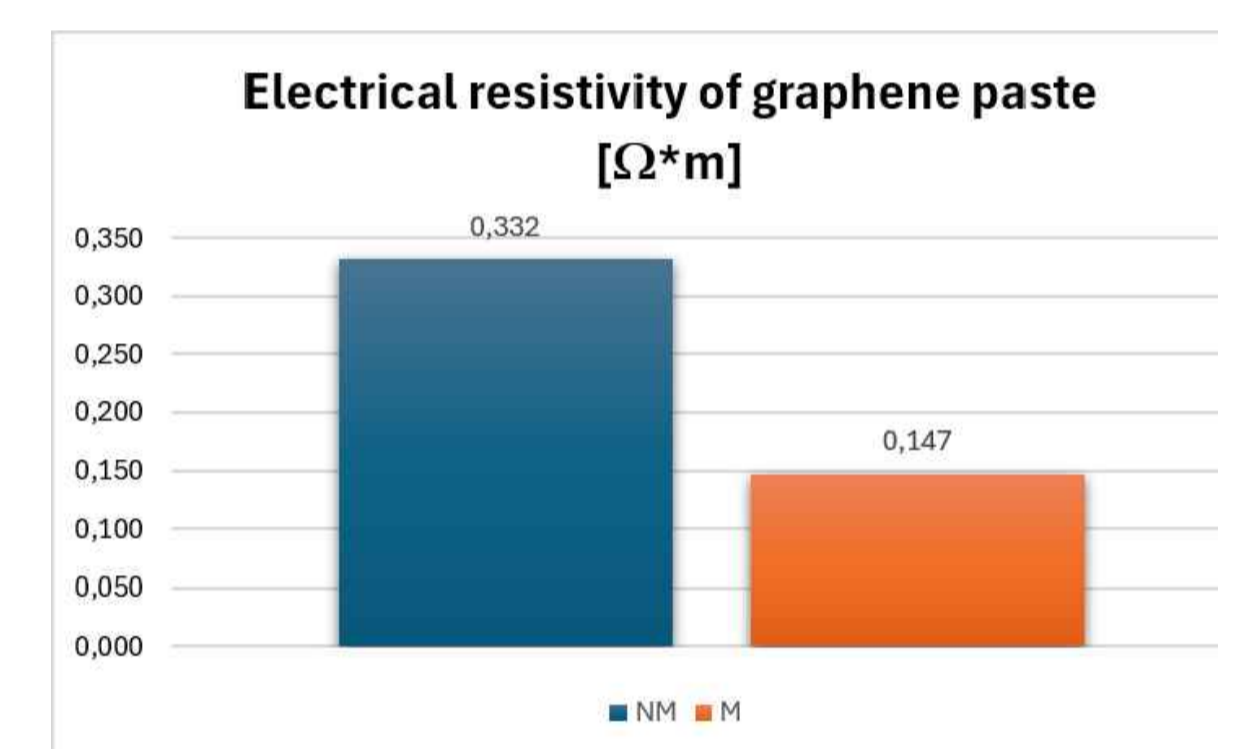


Fig. 11. Electrical resistivity evolution of fresh cementitious mixtures

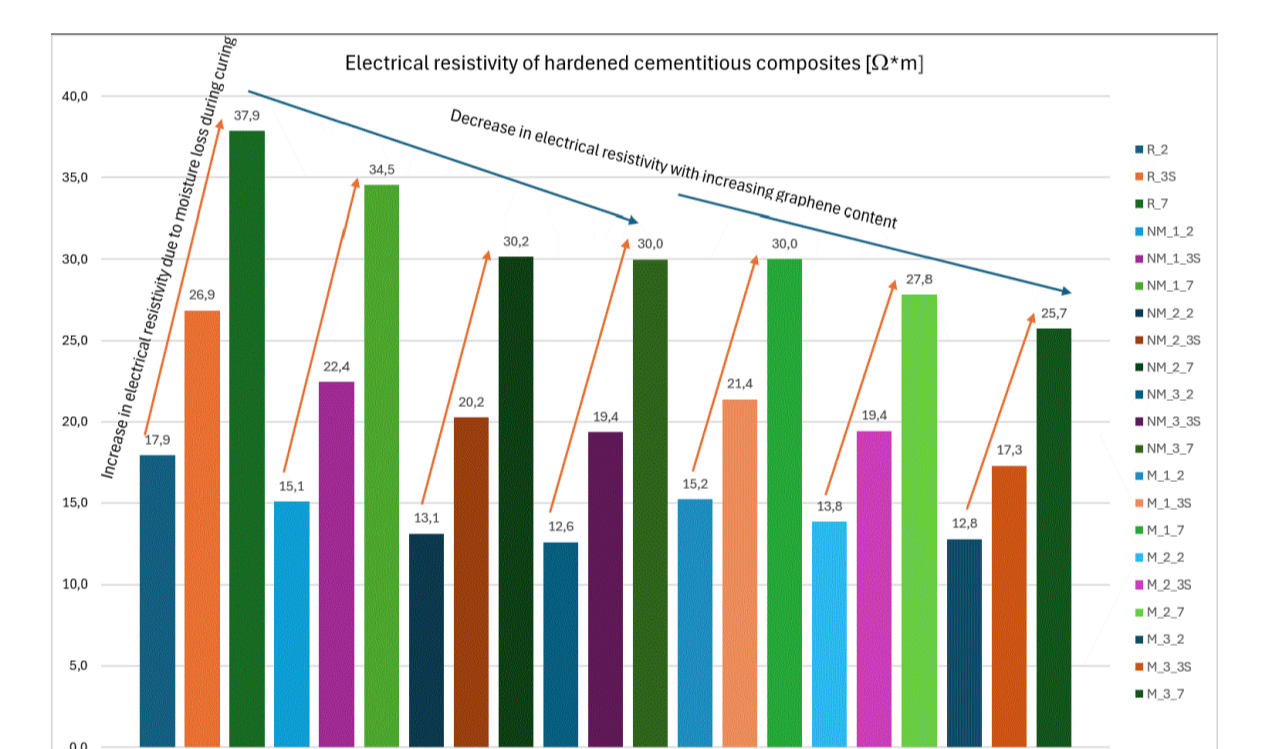


Fig. 12. Electrical resistivity of hardened cementitious composites

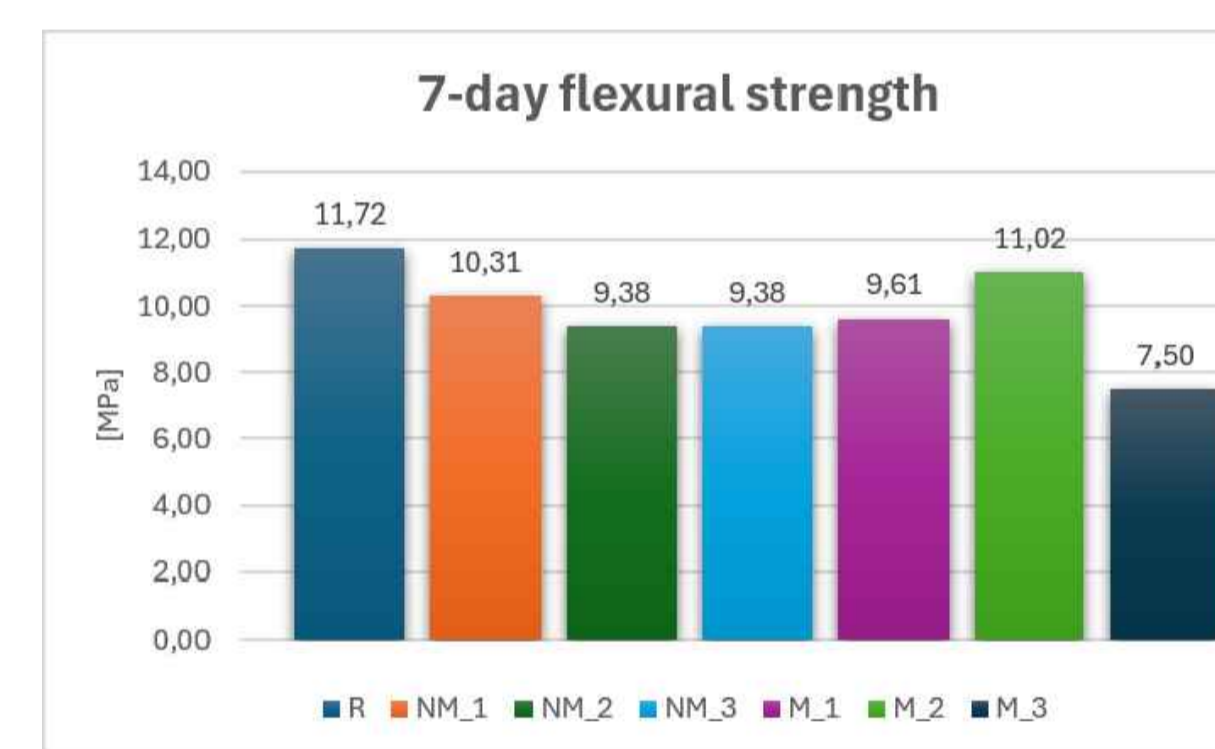


Fig. 13. 7-day flexural strength of cementitious composites.

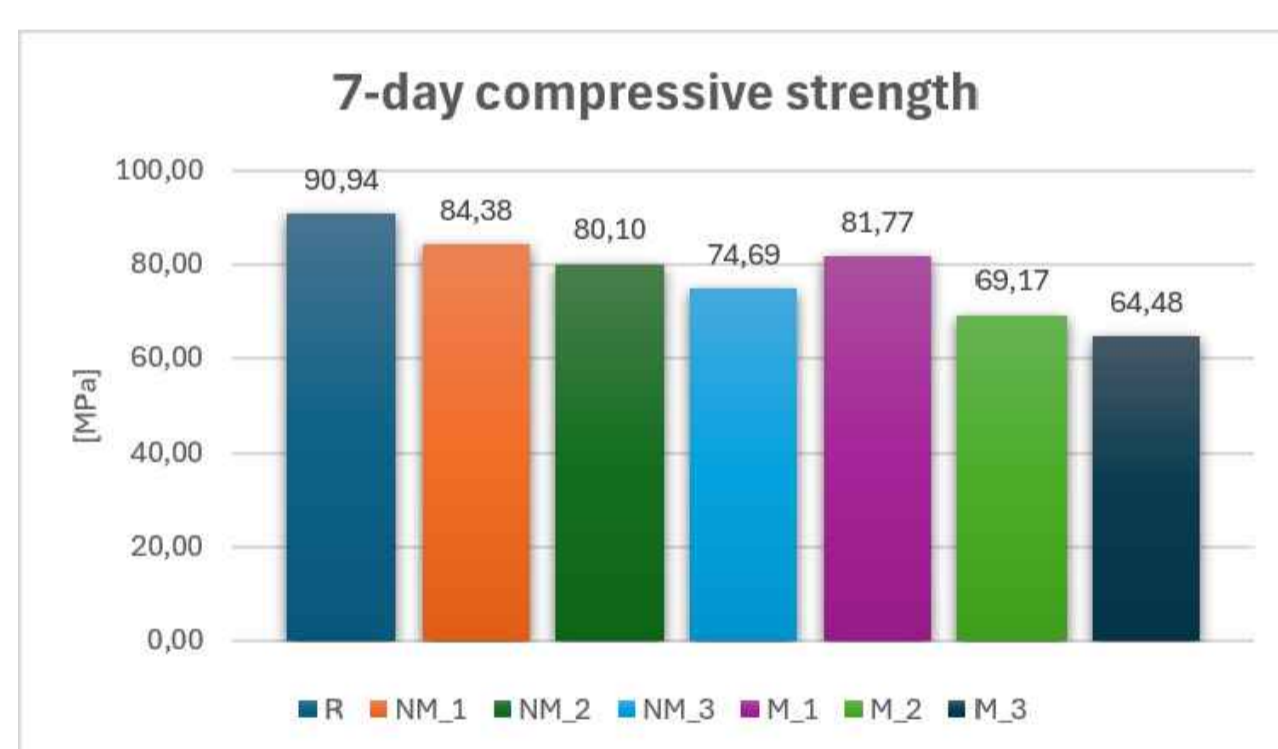


Fig. 14. 7-day compressive strength of cementitious composites.

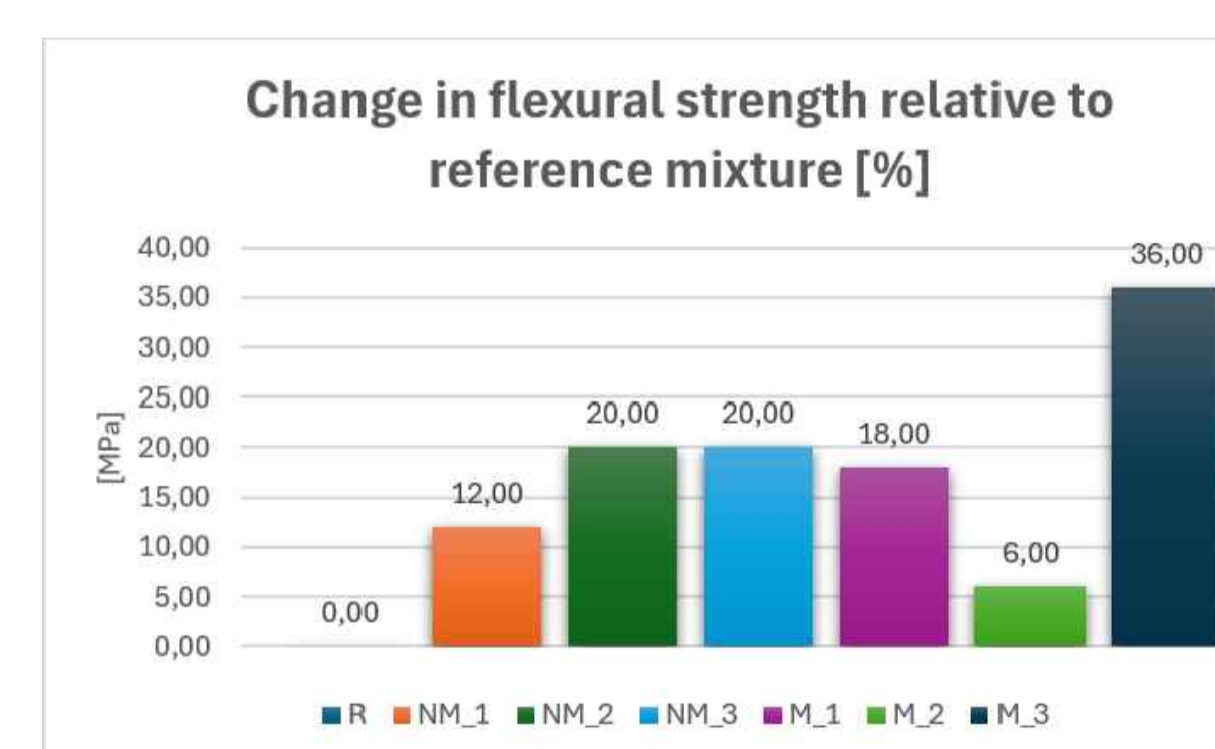


Fig. 15. Change in 7-day flexural strength relative to the reference mixture.

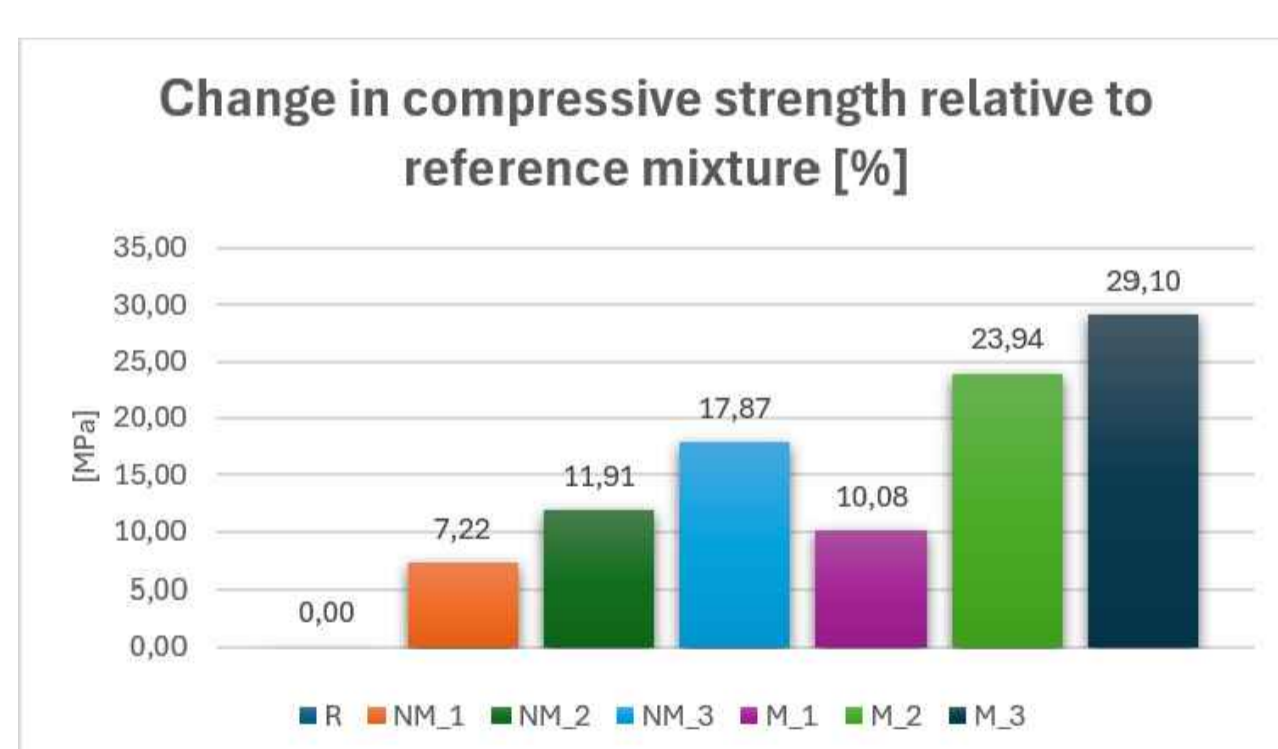


Fig. 16. Change in 7-day compressive strength relative to the reference mixture.

Discussion / Conclusions

The obtained results indicate that DBD plasma treatment affected the electrical properties of graphene paste. The pH of the graphene suspension decreased after modification, while the electrical resistivity of the paste was reduced from 0.332 Ω·m to 0.147 Ω·m, suggesting improved electrical performance of the modified graphene-based additive.

For fresh cementitious mixtures, electrical resistivity increased during the measurement period, which may be related to the early evolution of the cementitious system and changes in ion mobility. In hardened composites, resistivity increased with curing time, most likely due to progressive hydration and moisture loss. At the same time, higher graphene content generally contributed to lower electrical resistivity, indicating the gradual formation of conductive pathways within the cementitious matrix.

The mechanical results showed that the incorporation of graphene-based additives and ECAT reduced the 7-day flexural and compressive strength compared with the reference mixture. However, the obtained values remained at a satisfactory level, with flexural strength ranging from 7.50 to 11.72 MPa and compressive strength from 64.48 to 90.94 MPa. This suggests that the improvement in electrical properties can be achieved while maintaining good early-age mechanical performance.

Overall, the results confirm the potential of combining plasma-modified graphene paste with ECAT to develop cementitious composites with enhanced electrical functionality. Further research should include piezoresistive testing under mechanical loading to verify their suitability for self-sensing and structural health monitoring applications.

References and acknowledgements:

Wang et al. 2018; Vargas et al. 2024; Soriano et al. 2024; Michalek et al. 2026; Jin et al. 2023; Roshan et al. 2025. Selected graphical illustrations were generated with the assistance of ChatGPT (OpenAI) and reviewed by the author.