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Faculty of Chemical Engineering and Biotechnologies
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PhD Thesis

NANOPOWDERS USED IN BINDER MIXTURES FOR SPECIAL APPLICATIONS

- Resume -

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PART I – Literature Study

Inorganic binders are materials or mixtures of materials in powder form that, through interaction with water or aqueous solutions, undergo hydration-hydrolysis processes, forming systems that harden into solid, durable materials [1–4].

Binders can be classified based on several criteria according to: the nature of the binder (single or mixed binders), the method of production (non-clinkered and clinkered binders), and the hardening conditions (aerial and hydraulic binders).

Hydraulic binders are those that require a moist environment to harden and, after hardening, resist well in the presence of water [1–4]. Among these, the most important are those based on Portland or aluminous cement, either single or mixed.

Inorganic bio-binders are phosphate-based, and depending on their compositional characteristics, they are used in dentistry and hard tissue engineering.

Dental cements are essential materials in dentistry, used for fixing prefabricated restorations (crowns, bridges), temporary fillings, temporary or permanent cementing, and other applications. Among the various types of dental cements, inorganic phosphate bio-cements, which include zinc-phosphate, silico-phosphate, and calcium-phosphate cements, are well-known for their specific properties and diverse uses [5–11].

These systems solidify and harden through acid-base reactions, which are exothermic processes that form very stable salts in their working environment. They consist of a solid component, generally basic, and a liquid component, usually acidic. With the exception of calcium-phosphate systems, the setting time for these systems ranges from 4 to 10 minutes, and the mechanical compressive strength after 24 hours of application represents over 95% of the maximum value reached.

Zinc-phosphate cements are classic materials widely used in dentistry for cementing crowns and bridges [6–8,13]. From a chemical engineering perspective, these represent a fascinating example of composite material obtained through an acid-base reaction, with properties well-controlled by compositional characteristics and operational conditions.

Compositionally, zinc-phosphate cements primarily consist of two components: the solid phase—sintered zinc oxide powder (ZnO, with sintering additives such as MgO, SnO2, CaF2)—and the liquid phase—an aqueous solution of partially neutralized orthophosphoric acid (H_3PO_4, neutralizing agent: $Al_2O_3/Al(OH)_3$, ZnO). The aqueous solution of H_3PO_4 is typically in a concentration of 40-60%. Additionally, zinc oxide is known for its excellent biological properties.

Silico-phosphate cements represent a class of materials used in the medical field due to their unique properties, such as biocompatibility, durability, and mechanical performance [5,6,16].

Silico-phosphate dental cements consist of two components: the solid phase—an alumino-fluoro silicate glass powder—and the liquid phase—an aqueous solution of partially neutralized orthophosphoric acid (H_3PO_4, neutralizing agent: $Al_2O_3/Al(OH)_3$, ZnO). The aqueous solution of H_3PO_4 is typically at a concentration of 48-55%.

These cements exhibit high translucency, which is why they were initially called "dental porcelain." However, due to their solubility in the oral cavity over time, they become matte due to microcracking.

Silico-phosphate cements possess remarkable physicochemical and biological properties, such as: compressive strength (170-235 MPa), chemical stability (resistance to acid attack and chemical degradation, providing increased durability), adequate setting time (3(4)-24 min, which can be adjusted according to clinical needs by factors such as system composition, powder/liquid ratio, working temperature), and biocompatibility (they do not cause adverse reactions when in contact with biological tissues).

Calcium-phosphate cements (CPC) are biomimetic materials widely used in medical applications due to their biocompatibility, bioactivity, resorption ability, and capability to form new bone. Additionally, they can carry active pharmaceutical compounds, functioning as local drug delivery systems [6,18–27]. From a chemical engineering perspective, CPCs are of major interest due to their properties and ability to harden in moist environments, mimicking the natural behavior of bones. CPCs allow applications, particularly in minimally invasive surgery for bone defect reconstruction.

Acid-base hardening CPCs result from mixing with water or a diluted orthophosphoric acid solution (0.2%) of a powder formed from two phosphates—one more basic than hydroxyapatite and the other more acidic but with greater solubility than hydroxyapatite. At pH values corresponding to the physiological environment, after solidification and hardening, hydroxyapatite (apatite cement, AC) or dicalcium phosphate dihydrate (brushite cement, BC) forms.

Silico-calcium-phosphate cements are materials developed from calcium-phosphate cements and are used in hard tissue substitution and regeneration. These materials exhibit excellent bioactivity and osteogenicity.

They are produced by mixing calcium phosphates doped with Si4+ (e.g., TCP, DCPD) or their mixtures with calcium silicates (e.g., wollastonite, calcium orthosilicate, tricalcium silicate), either undoped or doped (e.g., Sr3+, Mg2+, Fe3+), with water or an aqueous orthophosphoric acid solution to primarily improve their physicomechanical and biological properties [26,32–38].

Various powders can be added to inorganic binder systems to improve their hardening behavior, with positive consequences for their physicomechanical properties and durability.

Recently, the development of nanotechnologies has enabled both in-depth characterization of these systems and the creation of micro- or nanocomposite binders with superior properties for special applications (e.g., in construction materials—self-cleaning binders, antibacterial materials, systems for monitoring crack propagation in mortar/concrete, and in biomedicine, particularly for enhancing biological behavior, such as antibacterial properties) [39–43].

Nanopowders are ultrafine particles ranging from 1 to 100 nanometers (nm) in at least one dimension. These particles, which fall under the category of nanomaterials, are distinguished by their extremely high specific surface area relative to their volume, giving them unique physical, chemical, and biological properties compared to bulk (macroscopic) materials of the same composition [44].

Thus, the main characteristics of nanopowders are [44]:

- Large specific surface area—This property increases chemical reactivity and interaction with the reaction environment, making nanopowders ideal for applications such as catalysis, sensors, or drug delivery.
- Unique optical, electrical, and magnetic properties—Due to quantum effects at the nanoscale, these materials can exhibit exceptional behaviors such as superconductivity, magnetism, or fluorescence.

- Potential to cross biological barriers—Their small size allows nanoparticles to cross cellular membranes, making them effective in targeted therapies and medical imaging.

PART II – Original Contributions

Motivation and Objectives of the Study

The aim of the undertaken study was to explore and highlight the advantages of using nanopowders within binder systems, with potential applications either in the field of construction materials with special uses or in the medical field, particularly in tissue engineering. Nanotechnologies have a significant impact on improving material properties, both in construction and biomedical applications.

The main objectives of the thesis were:

1. Development of special binder systems based on Portland cement with photocatalytic properties, containing ultrafine silica (UFS; a by-product from the ferroalloy industry, characterized by a large specific surface area and pozzolanic activity) on which TiO2 nanopowder (with photocatalytic properties) was deposited.

It was considered in the study that fixing the photocatalyst on the surface of a hydraulically active material would allow for better dispersion of the photocatalytic agent and improved stability. The sol-gel method was used for synthesis.

Both the individual components and the final composite materials were subjected to complex characterization using modern investigative techniques such as: thermal analysis, X-ray diffraction, electron microscopy (scanning and transmission), FT-IR and UV-Vis spectroscopy, specific surface measurements (Blaine and BET), and binder properties (standard consistency water, setting time, and mechanical strength).

2. Development of new bio-binder composites for medical applications, specifically for dental use in endodontics, for root canal filling or perforation filling, and dentin mineralization, using nanobio-cellulose (BC) and barium titanate (BT).

The main stages in obtaining these biomaterials were as follows:

i. Decomposition of the 3D porous structure of bacterial cellulose (BC), consisting of fibers and fibrils, through autoclaving treatment at 100°C for 24 hours in a basic medium (8M KOH), followed by grinding for 1.5 hours (150 rpm) in a planetary ball mill in an ethanol medium.
ii. Synthesis of barium titanate (BT) via the sol-gel hydrothermal method, where the gel was obtained from titanium butoxide and barium acetate, with a molar ratio of BaO = 1:1. Gelation occurred within 24 hours at room temperature, and drying was performed at 80°C for 24 hours. Hydrothermal treatment was carried out at 120°C for 24 hours in 4M KOH.
iii. Synthesis of silicate cement by thermal treatment at 1400°C for 2 hours and 1450°C for 4 hours of a precursor mixture obtained by the sol-gel method, followed by grinding for 30 minutes (150 rpm) in a dry medium in a planetary ball mill to obtain a fine white powder.
iv. Homogenization by sifting the silicate cement with BC or BT powder in a 9:1 ratio.

The addition of BC or BT to the cement aimed to improve its properties, from binder characteristics (setting time, mechanical strength) to biological performance.

Both the individual components and the final composite materials were subjected to complex characterization using modern investigative techniques, such as thermal analysis, X-ray diffraction, electron microscopy, specific surface measurements, and mechanical strength tests. Additionally, to demonstrate the applicability potential of the silicate cement-bio-cellulose or silicate cement-barium titanate materials, as well as their biocompatibility and bioactivity properties, in vitro tests were performed by immersion in simulated biological fluid (SBF) and behavioral evaluations in the presence of cell cultures (cell proliferation test – MTT and fluorescence optical microscopy, oxidative stress test - GSH).

3. Development of calcium silico-phosphate binder systems with the addition of nanobio-cellulose (BC) and/or barium titanate (BT), which can be successfully used in the substitution and regeneration of hard tissue, such as in endodontics for canal fracture filling.

These binders were obtained using a two-component system, consisting of:

- Solid component - calcium-silicate powders based on wollastonite with or without the addition of nanopowders (bio-cellulose and barium titanate), aimed at improving the binder's characteristic properties, particularly its biological behavior.

- Liquid component - aqueous phosphate solutions.

Both the individual components and the final composite materials were subjected to complex characterization using modern investigative techniques such as: complex thermal analysis, X-ray diffraction, electron microscopy (scanning and transmission), FT-IR and RAMAN spectroscopy, particle size distribution measurements, setting time, and mechanical strength tests.

General Conclusions and Originality

During the doctoral study, all proposed objectives were achieved, and all the materials obtained and examined for their properties demonstrated significant potential for application in fields such as construction materials or dentistry.

The doctoral study was divided into two main parts:

- Part I provided an overview of the importance of binder systems, the types of nanopowders used in construction materials with self-cleaning properties, or in tissue engineering, as well as the main synthesis methods for these materials.
- Part II presented an extensive account of the original contributions and the results obtained and disseminated in the specialized literature.

This structure allowed for a comprehensive exploration of both theoretical and practical aspects, showcasing the innovative potential of the research conducted.

Chapter 4 - Special-Purpose Construction Binder Systems with ultrafine silica (SUF) - TiO2 Powders

In Chapter 4, special binder systems based on Portland cement, incorporating ultrafine silica (SUF) and TiO2, were developed. The originality of this work lies in the fact that SUF was used as the surface on which TiO2 nanopowder was deposited. The chapter explored and developed the idea that fixing TiO2 on the surface of a hydraulically active material would enable better dispersion of the photocatalytic agent and improve its stability.

To demonstrate the initial hypothesis, both the individual components and the final composite materials were subjected to complex characterization using modern investigation techniques, including: Complex thermal analysis, X-ray diffraction Scanning and transmission electron microscopy, FT-IR and UV-Vis spectroscopy, Surface area measurements (Blaine and BET), Binder properties: standard consistency water, setting time, and mechanical strength.

The studied samples exhibited promising mechanical and photocatalytic properties through the addition of nanopowders, suggesting that these materials could be desirable solutions for self-cleaning construction materials.

The results obtained and presented in this chapter were reported in the paper "Synthesis and characterization of titania-silica fume composites and their influence on the strength of self-cleaning mortar" published in Composites Part B: Engineering in 2018 [155].

Chapter 5 - Biobinders of the Silicate-Clinker Type with ammonium phosphate, with and without Nanopowder Additives

Chapter 5 demonstrated the novel development of bio-binder composites with medical applications by using nano-powders such as bacterial cellulose (BC) and barium titanate (BT). The addition of nano-BC or nano-BT to the cement matrix aimed to enhance both the binder properties (setting time, mechanical strength) and the biological properties of the material. The potential applicability of silicate-bacterial cellulose or silicate-barium titanate cements, with a focus on biocompatibility and bioactivity, was highlighted through in-vitro tests, including immersion in simulated biological fluid (SBF) and behavioral evaluations in the presence of cell cultures (cell proliferation assay - MTT, optical fluorescence microscopy and oxidative stress - GSH).

Specific in-vitro tests (mineralization by immersion in SBF, MTT, GHS, and fluorescence microscopy) showed that all the studied materials have high applicability potential, with no adverse effects, making them suitable for integration into the human body for hard tissue substitution. Additionally, samples with BC or BT nanopowder additives demonstrated enhanced bio-efficiency.

Chapter 6 - Calcium Silico-Phosphate Biobinders with Improved Properties Through Nanopowder Addition

Chapter 6 focused on the novel development and analysis of calcium silico-phosphate binder systems with added nano-biocellulose (BC) and/or nano barium titanate (BT), with applications in grafting or repairing hard tissue, particularly for canal fracture treatment in endodontics. In-vitro tests and molecular biology studies showed that cells proliferate during contact with the obtained materials, and the studied genetic sequences indicated that materials with BC and BT generally promote the formation of mature osteoblasts.

The results obtained and presented in this chapter were reported in the paper "Modified calcium silicophosphate cements with improved properties" published in Materials Chemistry and Physics in 2019 [164].

Dissemination of Results

a) Publications in ISI-Cited Journals

1) **Zanfir, A.-V.;** Voicu, G.; Bădănoiu, A.-I.; Gogan, D.; Oprea, O.; Vasile, E. Synthesis and Characterization of Titania-Silica Fume Composites and Their Influence on the Strength of Self-Cleaning Mortar. Compos B Eng 2018, 140, 157–163, doi:10.1016/j.compositesb.2017.12.032 (Q1, FI2018=6,864).

2) **Zanfir, A.-V.**; Nenu, N.; Voicu, G.; Badanoiu, A.-I.; Ghitulica, C.-D.; Iordache, F. Modified Calcium Silicophosphate Cements with Improved Properties. Mater Chem Phys 2019, 238, 121965, doi:10.1016/j.matchemphys.2019.121965 (Q2, FI2019=3,408)

3) Pârvan, M-G.; **Zanfir, A.-V**.; Nicoară, A-I.; Voicu G. Influence of different synthesis routes on barium titanate powder characteristics, U.P.B. Sci. Bull., Series B, 83 (2), 95-104, 2021, ISSN 1454-2331, WOS: 000661663200010.

Journal	**Impact factor**
Composites B	6.864
Materials Chemistry & Physics	3.408
Factor de impact cumulat	**10.262**

b) Presentations at National/International Conferences

- **Zanfir, A.-V.**; Voicu, G; Bădănoiu, A.-I.; Gogan, D.; Oprea, O.; Truşcă, R. The coating of silica fume with titanium oxide nanoparticles and the effect on photocatalytic and pozzolanic activities, S6-124, 20th Romanian International Conference on Chemistry and Chemical Engineering (RICCCE 20), 6-7 September, 2017, Brasov, România.

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