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REVIEW OF DOCTORAL THESIS

M.Sc. Eng. Agnieszka Antończyk

„Development of the silanization proces for spherical aluminosilicates dedicated as filler for polymers used in medical devices."

Supervisor: Witold Walke, PhD, DSc., Associate Professor

Auxiliary supervisor: Magdalena Antonowicz, PhD

Basis for the Review Preparation

The review was prepared at the request of the Chairman of the Biomedical Engineering Discipline Council at the Silesian University of Technology on October 17, 2024 (Resolution No. 75/2024).

Reviewed doctoral thesis of M.Sc. Eng. Agnieszka Antończyk was performed under the supervision of Witold Walke, PhD, DSc., Associate Professor and the auxiliary supervisor is Magdalena Antonowicz, PhD. The doctoral dissertation is in the discipline of biomedical engineering, and specifically concerns bone cements and fillers used for implantation.

Characteristics of the research subject and the aim and scope of the work

Bone cements are materials that connect the implant to the bone and are also used to fill them, e.g. after resection. They are used in hip and knee alloplasty, but also in other reconstructive procedures. They may contain additives, e.g. antibiotics (gentamicin, vancomycin) or metal nanoparticles with biocidal properties.

The tissue replacement material must have appropriate properties: biocompatibility and be characterized by appropriate mechanical and physical parameters. Biomaterials can be given appropriate properties that favor the process of bone reconstruction and reduce the possibility of infections. The body's rejection of the implant is a direct result of the lack of osteointegration of the implant surface with the bone.

The subject of the reviewed doctoral thesis is: development of a silanization process for spherical aluminosilicates dedicated as a filler for polymer composites used in medical devices. The substantive scope of the work is very important, and the reasonableness of the research topic undertaken is important for biomedical engineering. The results obtained, presented in this paper, are of great scientific and utilitarian importance for the further development of biocompatible materials used in medicine.

The title of the work is consistent with the research topic and the content included in the dissertation. The aim of the dissertation is to develop a silanization process for spherical aluminosilicates in order to obtain amino, carboxyl and nitrogen groups that improve their adhesion to the matrix in bone cement.

Based on literature studies, the PhD student created a research thesis regarding alternative solutions for currently used fillers in bone cements, developed during the silanization process of spherical aluminosilicates, so as to enable their permanent chemical and physical bonding with the polymer matrix in composite materials.

The purpose of the work is clearly formulated and the thesis is correct.

The scope of the doctoral thesis is coherent and closely related to the topic. It is shown graphically (Fig. 16, p. 40). Its detail should be emphasized.

Scope and evaluation of individual parts of the work carried out

The reviewed doctoral dissertation is written in English and contains 109 pages, including an abstract in Polish and English. The layout of the work is correct, typical of experimental work.

The introduction justifies the origins of the research topic, the validity of conducting the research and presents the structure of the work.

The work is divided into a theoretical part, containing a detailed literature analysis - 97 items, mostly in English, related to the subject of the work. At the beginning, the author briefly introduces the diseases of the skeletal system, and then goes on to describe bioceramics - bone cement, as well as fillers and methods of improving the adhesion of ceramic materials with a matrix of polymeric materials.

The second part of the work concerns research conducted by the PhD student.

Currently, a big problem is ensuring good bonding at the material-tissue interface. The author proposed ceramics in the form of aluminosilicates as a filler for commercially used bone cement. This is intended to improve implant fixation in bone surgery and as a material for bone reconstruction.

A huge problem with bone cement is the high temperature during polymerization, which can cause damage to bone tissue (necrosis). Numerous modifications are introduced for better adhesion of cement to bone. Their main purpose is to improve the adhesion of osteoblasts to the implant and to be biocidal (antibiotics, nanometals), which prevents the formation of a biofilm.

In the Materials chapter, you will find a description of the basic, most frequently used ceramic fillers, spherical aluminosilicates, which do not have a toxic effect on tissues, and the silanization process - which improves adhesion.

Then, the PhD student showed a detailed research plan in the form of a diagram (Fig. 16, p. 40), with a detailed description of the subsequent tests, including the course of the silanization process.

The work contains several research methods used at a later stage in the research (thermogravimetric analysis, particle size, phase composition, infrared spectroscopy analysis with Fourier transform, analysis of microstructure, porosity, polymerization temperature,

wettability, mechanical properties, static tension, static uniaxial compression test , static three-point bending test, biological-cytotoxicity). Thanks to them, among others, the microstructure analysis showed that a uniform distribution of elements has a positive effect on the chemical bond with the matrix, and that the bone cement before and after modification with aluminosilicate penetrates the cement into the bone pores, which may indicate good adhesion of the material to the bone. However, the wettability test showed the hydrophilicity of the material, which favors the adhesion of osteoblasts. The use of the filler after modification with silicon resulted in an increase in the contact angle. This is caused by a change in the structure of the cement, i.e. a reduction in the proportion of pores.

The multitude of research methods and research results as well as their detailed description and analysis make the work of great practical and scientific importance.

Editorial notes

The PhD student did not avoid stylistic errors in her work, in some places there are missing commas or, as is the case on page 29, lack of literature support (marked with 3 dots). The graphs (e.g. Fig. 84) are difficult to see and should be enlarged. However, when it comes to the bibliography, I did not note the date of access to online sources. The literature also does not include any items with the participation of the author of the dissertation.

Overall assessment of the work

The aim of the work was to develop a silanization process for spherical aluminosilicates in order to obtain amine, carboxyl and nitrogen functional groups in order to improve their adhesion to the matrix compared to those currently used in bone cements. For research, the PhD student chose: aluminum oxide (Al2O3), zirconium oxide (ZrO2) and spherical aluminosilicates with fractions (C90, C150, C212). Then, each material was subjected to the silanization process. After this process, the samples underwent detailed tests, and their description was included in the results and an extensive discussion. The aim of the dissertation was achieved, and I rate the substantive part of the work highly.

After analyzing all the tests performed, the author showed that modification with silicon nitride is the best variant for further modification to create a new type of bone cement based on spherical aluminosilicates. The dissertation showed that the layer created on the surface of spherical aluminosilicates in the silanization process allows designing a surface with properties similar to those of the bone tissue environment.

Final conclusion

To sum up, I believe that the doctoral thesis of Ms. M.Sc. eng. Agnieszka Antończyk's work is scientific and original. It is a significant contribution to biomedical engineering, especially in the area of research on modern biomaterials. In the dissertation, the author demonstrated experimental skills.

To sum up, I say that the doctoral dissertation of Ms. M.Sc. Eng. Agnieszka Antończyk, entitled: "Development of the silanization process for spherical aluminosilicates dedicated as filler for polymers used in medical devices", meets the requirements specified in the Act of July 20, 2018 - Law on Higher Education and Science (consolidated text: Journal of Laws . of 2023, item 742, as amended), in the discipline of biomedical engineering.

I am applying for the acceptance of the doctoral dissertation of Ms. M.Sc. Eng. Agnieszka Antończyk and allowing her to defend herself publicly.

Podpisała Beata Świeczko-Żurek (podpis odręczny)

The work is written in correct language, and the formulated content does not pose any problems with reading fluency. The figures are well analyzed in the text. Minor stylistic errors do not detract from the dissertation. The research methodology is very good, and the literature is appropriately selected to the topic of the work. The layout of the dissertation is appropriate for a doctoral thesis. The overall assessment of the work shows that the work is original and substantively coherent.

The PhD student demonstrated theoretical knowledge and commitment to conducting scientific research in the discipline of biomedical engineering.

The most important achievements of the PhD student include:

1. The aim of the study was defined correctly, and the results obtained can be the basis for further in vivo and in vitro research.

2. Research conducted by the PhD student showed how to modify the surface of spherical aluminosilicates, enabling their introduction as a filler into PMMA.

3. The samples were subjected to 13 research methods, from which conclusions were drawn and an extensive discussion was held, also based on literature.

Please, refer to the following issues:

1. Was there any publication regarding the research described in the dissertation during the PhD period? In the literature attached to the dissertation, I did not find any publications with the author's participation (neither under her maiden name Dubiel nor under the currently used Antończyk).

2. The disadvantage of cements stabilizing implants in the bone is the appearance of a gap between the cement and the implant. This gap is the result of polymerization and thermal shrinkage after lowering the temperature. The gap becomes overgrown with fibrous tissue, but this process reduces the stiffness of the cement-implant connection, which increases the risk of cement cracking. Did you take this into account when researching fillers?