Doctoral thesis review

Title:	Development of the Silanization Process for Spherical Aluminosilicates Dedicated as Filler for Polymers used in Medical Devices
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General evaluation:

The presented work deals with the very current issue of improving the properties of cements used in medicine. These cements are filled with different types of particulate fillers, which have to show good adhesion to the cement matrix. To achieve sufficient adhesion, modification of the fillers surface is necessary and Agnieszka Antoczyk focused on the silanization of the surfaces of the selected fillers with a special focus on the aluminosilicate fillers. The issue addressed is undoubtedly very current.

The objectives of the experimental part of the thesis are clearly mentioned in Section III *Research* (page 39), and after studying the thesis, I assess that the stated objectives have been met.

The thesis, written in a total of 109 pages, is structured into four main chapters, Introduction, Literature review, Research, and Bibliography. The two main chapters are 'Literature review' and 'Research'. The literature review chapter is written in a clear way and allows those who are not familiar with the field of medical cements to understand the subject. Each of the chapters contains a short summary at the end, in the case of the Research chapter, this chapter is labelled 'Conclusion'. Personally, I would have chosen a different title and I would have recommended the 'Conclusion' chapter to be included separately on the main level. In addition to a summary of the results and their contributions so far, the 'Conclusion' chapter should also contain recommendations for further research activities in the study area. I positively evaluate the inclusion of Figure 16, which clearly describes the structure of the research work itself.

The core of the thesis is the chapter 'Research'. The author focused on the evaluation of the possibility of using spherical alumininosilicates as a filler of cement based on PMMA, with special focus on silanization of the surface of this filler. As a reference, Al_2O_3 and ZrO_2 fillers were used. The surface modification was carried out using three silanization agents – Si_3N_4, (3-aminopropyl)-triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS). The modified fillers were characterized using various methods of chemical and phase analysis, thermal

analysis, and scanning electron microscopy. I miss the comparison of the results with pristine (nonmodified) fillers.

The following subchapter (5.8) focuses on the characterization of prepared bone cements. I negatively evaluate the absence of a text that would clearly recapitulate what filler was used for the preparation of the samples and why. Although later it was clear from the text that the sample was C150, it is not clear which compound was used to modify the surface of this filler. In this chapter, the designations of samples A, B, C and D are given, but the composition of these samples is nowhere recapitulated, nor is the meaning of the designations CK and GK. These shortcomings make it difficult to navigate this part of the text.

Tables are of appropriate quality and provide information in the text. Unfortunately, some of the figures are of low quality, for example Figure 25, and it is really hard to read the values on the axes. Another problem is the numbering of the figures, which sometimes does not follow each other, for example, Fig. 172, which follows Fig. 31. The thesis includes citation to 97 references, distributed within the chapters focused on theoretical, and also experimental parts.

Evaluation of all the data obtained led to the important finding that spherical aluminosilicates are suitable fillers for bone cements. I also consider very important the inclusion of cytotoxicity tests, which showed lower LDH levels for samples filled with 30 and 40% aluminosilicate filler compared to a single cement without filler.

In the dissertation submitted, Agnieszka Antończyk presented spherical aluminosilicates as a promising type of novel bone cements fillers. The results obtained indicate that this kind of filler is suitable for this purpose. The stated results and findings are good pillars for future research activities in the field of bone cements.

I have following comments, questions:

1. On page 27, there is the comment, 'A key property of spherical aluminosilicates is that they have no harmful effects on living organism, allowing them to be considered as a material for use in human products'. On previous page, there is the information, that aluminosilicates microspheres can contain Cu, Ni, Pb, Zn, and Cr. Regarding the possible content of these heavy elements, could the silanization process be considered as the method for creating a surface barrier for these elements?
2. Why does the author discus the results of the TG analysis (page 53) in relation to thermal stability of kaolinite? Is the kaolinite phase typical in spherical aluminosilicates?
3. In my opinion, the images in Figure 63 show the porous structure of the hardened bone cement samples, but in Chapter 5.7 'Porosity studies' is mentioned, that the samples are non-porous. It is necessary to provide information on sample preparation for N_2 physisorption experiment.

4. An important parameter of bone cements is their wear resistance. How could the wear resistance be evaluated?

Although I have some critical remarks about this work, which I have raised earlier, I consider the submitted thesis as a proof that mgr inž. Agnieszka Antończyk is capable of independent creative work, she is able to analyze the information from the literature and, on their basis, is able to propose the plan of the experiments, conduct the experiments, and analyze the results obtained.

To sum up, I state that the presented doctoral dissertation of Agnieszka Antończyk, M.Sc., Eng., meets the conditions set out in Article 187 of the Act of 20 July 2018. Law on Higher Education and Science (Journal of Laws of 2024, item 1571). Therefore, I am requesting that you be admitted Agnieszka Antończyk, M.Sc., to further stages of the doctoral dissertation.

in Ostrava 12.12.2024

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