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Review

The doctoral dissertation of MSc Eng. Agnieszka Antończyk entitled "Development of the Silanization Process for Spherical Aluminosilicates Dedicated as Filler for Polymers used in Medical Devices" is an extensive and multi-faceted scientific study consisting of over 100 pages and containing numerous chapters that systematically describe the research issues, methodology, results, and discussion. The entire work is divided into thirteen main chapters, which include a literature review, detailed descriptions of experiments, and analysis of results.

The literature part of the work of MSc Eng. Antończyk emphasizes the scientific significance and potential impact on the development of biomedical and materials engineering. The author conducted extensive research on the silanization process of spherical aluminosilicates, used as fillers in polymer composites used in medical devices. This problem was identified based on an extensive literature review, which indicates the limitations of currently used filler materials, such as aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2). Despite their good mechanical properties, these materials are often characterized by insufficient adhesion to polymer matrices, which can weaken their functional properties and the formation of microcracks. In the theoretical chapters, the author presents the current state of knowledge on ceramic biomaterials and their role in medicine, indicating the potential applications of spherical aluminosilicates as an alternative filler. She describes the processes of their formation, physical and chemical properties, as well as potential applications in engineering biomaterials. She emphasizes the importance of their unique structure and lightweight structure, which makes them potentially ultralight fillers with high strength. The literature review included in the doctoral thesis indicates the interdisciplinarity and relevance of the subject. The author relies on numerous scientific publications that discuss both the general properties of ceramic filling materials and detailed techniques for improving their adhesion to polymer matrices. Silanization is a key process in the research of MSc Eng. Antończyk, is discussed in detail, taking into account the

properties of silane compounds, such as 3-aminopropylethoxysilane (APTES) and tetraethoxysilane (TEOS), and their ability to form bonds with material surfaces. The author describes in detail the chemical mechanisms occurring during silanization, making her work an important source of knowledge for researchers and engineers working on developing biomaterials. The experimental part of the work is also extensive and includes a description of analysis methods, such as thermogravimetric analysis, chemical composition studies, particle size analysis, infrared spectroscopy (FTIR), microstructure studies, and tests of mechanical properties of bone cement. The author's research results confirmed that the use of spherical aluminosilicates as a filler in polymer composites improves their adhesive properties, which is consistent with theoretical data. In the theoretical part of her doctoral thesis, MSc Eng. Agnieszka Antończyk conducts a comprehensive literature analysis and a detailed discussion of the scientific basis that constitutes the foundation of her research on modern ceramic fillers in polymer composites. The theoretical part of the work consists of six chapters, which together build the scientific basis for the presented research.

Chapter 1 serves as an introduction to the subject of the work, focusing on the analysis of problems related to bone diseases and disorders, such as osteoporosis and fractures, especially in the femoral neck. The author presents epidemiological and statistical data that emphasize the commonness of these diseases and their negative health and economic consequences. She also indicates the need to develop innovative material solutions that can significantly improve the quality of treatment and the long-term effects of patient recovery. This chapter introduces the reader to the broader clinical and social context, justifying the importance of research on modern biomaterials used in medicine.

Chapter 2 focuses on a detailed discussion of using bone cements as materials to fill bone defects and stabilize prostheses in the stomatognathic system. The author describes different types of bone cements, with particular emphasis on polymethyl methacrylate (PMMA), one of the most commonly used materials in this field. It also presents the key physical and chemical properties of bone cements, as well as the polymerization processes that can affect their durability and biocompatibility. Both the benefits of using these materials and their limitations are analyzed, such as the possibility of inducing local inflammatory reactions or weakening the surrounding bone tissue.

Chapter 3 concerns a detailed analysis of the use of ceramic materials as fillers in bone cements. In this chapter, the author discusses the properties of ceramics, such as aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2), characterized by good biocompatibility and high mechanical strength. The author emphasizes that despite these advantages, these materials have their limitations, primarily in terms of adhesion to polymer matrices. Poor adhesion can lead to microcracks and weakening of the composite structure, which limits their clinical use. The author also presents strategies to increase the adhesion of ceramic materials, preparing the ground for the discussion of the use of surface modification in the following chapters.

Chapter 4 is devoted to spherical aluminosilicates, which the author considers potential polymer composites fillers. This chapter describes in detail the process of aluminosilicate synthesis, their unique chemical and physical structure, and their potential applications in biomaterials. Antończyk explains that due to their spherical structure and lightweight structure, aluminosilicates can be a promising ultralight filler that not only improves the mechanical properties of composites, but can also reduce the load on the material structure. The author compares the properties of aluminosilicates with traditional ceramic fillers, emphasizing their advantage in the context of chemical modification possibilities.

Chapter 5 focuses on surface modification methods to improve the adhesion of ceramic materials to polymer matrices. The work describes in detail the silanization process and the mechanisms of action of silane compounds such as 3-aminopropylethoxysilane (APTES) and tetraethoxysilane (TEOS). The author discusses the chemical reactions occurring on the surface of aluminosilicates during the silanization process, which allow for the introduction of functional chemical groups capable of creating permanent bonds with polymers. This chapter also presents literature studies that confirm the effectiveness of this type of modification in increasing the adhesion and strength of composite materials.

Chapter 6 summarizes the theoretical part, in which the author collects and synthesizes the information discussed earlier. She emphasizes the limitations of existing material solutions and argues for the need to conduct further research on the use of spherical aluminosilicates as innovative fillers. Antończyk indicates the potential benefits of using silanization to improve adhesion, which is crucial for the practical application of these materials in biomedical engineering.

The theoretical part of the work of MSc. Eng. Agnieszka Antończyk is comprehensive, scientifically justified, and provides a solid basis for the experimental part, which examines the proposed solutions in practice following the previously presented goals of the work.

In the research part of the doctoral thesis, MSc. Eng. Agnieszka Antończyk carried out a detailed analysis and implementation of the research goals, which aimed to develop modern methods of improving the adhesive properties of ceramic fillers through the silanization process. The work includes five key chapters describing a comprehensive approach to the implementation of experiments, from the materials selection through surface modification methods to a detailed analysis of the obtained results.

Chapter 1: Research goals and hypotheses - The author formulates the main goal of the work, which consists of developing an optimized silanization process of spherical aluminosilicates, enabling the obtaining of functional groups such as amine, carboxyl, and nitrogen groups. The aim is to increase the adhesion of these fillers to the polymer matrix, leading to the improvement of mechanical properties and durability of composites used in medical devices. The hypotheses assume that the introduction of surface modification of aluminosilicates will allow for a more homogeneous and stable structure of composites and minimize the risk of microcracks. The author suggests that selected silanization methods can significantly increase the adhesion between the composite phases, which was verified in experiments.

Chapter 2: Research materials and methods – This chapter describes in detail the sample preparation procedures and the selection of materials used for the research. The author focused on spherical aluminosilicates with a fraction C90, C150, and C212, as well as conventional materials such as aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2). Methods for the preparation and modification of filler surfaces are presented, including the use of silane compounds such as 3-aminopropylethoxysilane (APTES) and tetraethoxysilane (TEOS), and chemical methods such as the use of silicon nitride (Si_3N_4) in combination with sodium hydroxide (NaOH). This chapter also describes in detail the processes of preparing samples for analysis and the research methodology, including both laboratory tests and chemical and physical analyses.

Chapter 3: The process of manufacturing polymer composites - This chapter is crucial for understanding the research methodology. The author describes the composite synthesis processes, including precise mixing of modified fillers with a polymer matrix based on polymethyl methacrylate (PMMA). Particular attention was paid to the curing and

polymerization conditions, as well as the control of temperature, reaction time, and mixing parameters to ensure a uniform distribution of particles throughout the matrix. The presented procedures aimed to obtain composites with optimized mechanical strength and increased chemical stability.

Chapter 4: Research results and analysis - Antończyk presents in detail the results obtained during the research, which include various analyses such as thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR), particle size analysis, microstructural studies using electron microscopy and mechanical tests, including compressive, tensile and bending strength tests. The results indicate that the introduction of modified aluminosilicates leads to increased adhesion and improved mechanical properties of the composites. Particularly good results were obtained for aluminosilicates with a fraction of 150 μm, which were silanized using Si_3N_4 and NaOH, which showed significant changes in the chemical structure of the surface and its properties.

Chapter 5: Cytotoxicity assessment and biological studies – The last research chapter contains the results of biological tests, including the assessment of cytotoxicity of the obtained composites. These studies aimed to assess the safety of contact between materials and bone tissue and their potential application in medicine. The results showed no significant cytotoxicity, which suggests that the developed composites can be safely used in clinical applications, potentially constituting a better alternative to traditional fillers.

To sum up, the research part of the work of MSc Eng. Agnieszka Antończyk fully confirms the hypotheses and achieves the scientific goals. The studies have shown that the use of surface modification through the silanization process increases the adhesion between the filler and the matrix, which translates into better mechanical properties of the composites. This work makes a significant contribution to the development of modern biomaterials, which can be used in clinical and industrial practice.

In the doctoral thesis of MSc Eng. Agnieszka Antończyk, the discussion and conclusions are key elements of the analysis of the results obtained during the conducted research and the assessment of the hypotheses.

The discussion in Antończyk's dissertation is detailed and substantive, based on the results of research on the use of spherical aluminosilicates in polymer composites and their modification by the silanization process. The author compares the results of her own research with the existing literature, emphasizing the innovativeness of her method. In the discussion, she

discusses the effectiveness of the applied surface modifications, which allowed for the improvement of the adhesion of ceramic fillers to the polymer matrix, which translated into better mechanical and chemical properties of the composites. The discussion of the results is solidly supported by the analysis of research data, such as SEM, FTIR, XPS and mechanical tests, which provides a comprehensive understanding of the obtained results. In the discussion, the author emphasizes that the surface modification of aluminosilicates with Si_3N_4+NaOH, APTES and TEOS was crucial for achieving the desired properties of the materials. Further comparisons with the results from the literature indicate the advantage of her method over traditionally used fillers, such as aluminum oxide and zirconium oxide. The discussion also includes an analysis of the limitations of the research, such as the influence of various process parameters on the result of surface modification, which is important for future research. The conclusions of the work are precisely formulated and demonstrate consistency with the hypotheses and objectives of the work. Antończyk concludes that the developed silanization process enabled permanent chemical and physical connection of aluminosilicates with the polymer matrix, which is an alternative to traditional fillers used in bone cements. She indicates that surface modification leads to increased adhesion and mechanical strength of composites, which was confirmed by strength tests and surface morphology analysis.

Conclusions, such as confirmation of the presence of functional chemical groups (amino and carboxyl) on the modified surfaces and their effect on the adhesive properties are clearly correlated with the research hypotheses presented in the work. The results of cytotoxicity tests showed the safety of the developed materials, which opens the possibility of further research on the clinical applications of these composites. To sum up, the discussion and conclusions in the work of MSc Eng. Agnieszka Antończyk is appropriately constructed, logical, and based on solid experimental data. The work proves that the goals and hypotheses have been realized, and the presented results can have practical applications in biomedical engineering, which indicates the high substantive and application value of the work.

In the doctoral thesis of MSc Eng. Agnieszka Antończyk, one can notice several aspects that could be discussed in more detail, as well as potential shortcomings and limitations in interpreting the results. Below I present an elaborate analysis of these elements.

The first aspect that would be worth deepening is the detailed analysis of the effect of individual parameters of the surface modification process on the final properties of modified aluminosilicates. In the paper, the author describes the silanization process and chemical modification methods, but a discussion of the influence of parameters such as reaction time,

temperature, reagent concentration, or mixing method on the effectiveness of modification could significantly enrich the conclusions of the research. A precise analysis of these variables would allow for a better understanding of which factors have the greatest impact on achieving the desired adhesive and mechanical properties of composites. Such an extension of the research would provide valuable information for future applications and could serve as a guide for researchers working on similar projects. Another important element is the comparison of the results obtained for aluminosilicates with the results for other, traditionally used filling materials, such as aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2). The dissertation contains a comparative analysis, but a more detailed discussion of the differences in strength, adhesion, biocompatibility, and other mechanical properties between these materials and the new fillers could enrich the scientific context of the work. Such an extensive review would help to better determine the real advantages of aluminosilicates over other materials and provide more convincing evidence for their clinical potential. The interpretation of cytotoxicity test results also deserves a more detailed discussion. The author presented the results of cytotoxicity tests, which confirmed the biological safety of the tested materials, but a more in-depth statistical analysis of these data, paying attention to the statistical significance of the differences between the samples, could strengthen the credibility of the conclusions. Statistical analysis, taking into account standard deviations and significance tests, would allow for an unambiguous determination of whether the observed differences are statistically significant, which would be of significant importance for potential clinical applications. In terms of conclusions regarding the clinical usefulness of the work, it would be worth adding a more extensive discussion of the steps that should be taken before implementing the developed composites in medical practice. The author mentions the potential use of biomaterials in medicine, but a more detailed indication of further studies, which should include in vivo tests, could contribute to making the presented application perspectives more realistic. Such a suggestion could also serve as a reference point for future researchers who would like to continue working on the implementation of these composites in clinical practice. Although the conclusions of the work are well-constructed and correlated with the presented goals and hypotheses, a more critical approach to interpreting the results could be considered. The author could have discussed in more detail potential methodological limitations, such as the influence of environmental variables on the efficiency of the silanization process and the properties of the composites. Such a discussion would indicate an awareness of the complexity of the process and could contribute to a more comprehensive assessment of the obtained results. The lack of errors in the interpretation of the results suggests that the author has carefully analyzed and presented the

results, but the expansion by discussing potential uncertainties or possible deviations in the methodology would have helped to better understand the results and their significance. For a more complete picture, it would also be worth including an analysis of the impact of possible limitations related to the diversity of surface modification methods and their repeatability on an industrial scale. In summary, although the work of M.Sc. Eng. Agnieszka Antończyk is reliable and well prepared, its value could be increased by a more detailed discussion of the influence of process parameters, an extension of the comparative analysis with other materials, a detailed statistical analysis of cytotoxicity results, and in indicating further directions of research in the field of clinical implementation. Such expansion could make the work even more comprehensive and helpful for other researchers in the field of biomedical engineering. The doctoral dissertation of MSc Eng Agnieszka Antończyk entitled "Development of the Silanization Process for Spherical Aluminosilicates Dedicated as Filler for Polymers used in Medical Devices" is an independent and carefully thought-out research work that makes a significant contribution to the development of modern biomedical materials. The work was written in a logical and transparent manner, leading the reader through subsequent stages of the literature review, research methodology, and analysis of results. The author has demonstrated scientific maturity and a critical approach to discussing the obtained results, which confirms her high competence in the field of materials and biomedical engineering. The doctoral student conducted comprehensive research on the silanization process of spherical aluminosilicates, analyzing their effect on the adhesive and mechanical properties of polymer composites used in medical devices. The research results indicate that surface modification using appropriate silane compounds contributed to increased adhesion of fillers to the polymer matrix, which translated into improved mechanical strength and chemical stability of the composites. The results of cytotoxicity tests also confirmed the safety of the developed materials, which suggests their potential use in medicine. The work of MSc Eng. Agnieszka Antończyk meets the statutory criteria of the conditions specified in art. 187 of the Act of 20 July 2018 - Law on Higher Education and Science (consolidated text Journal of Laws of 2020, item 85, as amended), and therefore I request that the PhD student be allowed to present her public defense.

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