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REVIEW OF THE DOCTORAL DISSERTATION

MSc. Eng. Cesar Israel Hernandez Vazquez

„Assessment of the effects of various carboxylic acids as solvents, characterization and enhancement of mechanical and antibacterial properties of wet-spun chitosan fibres”

Doctoral dissertation promoter: Zbigniew Draczyński PhD, Eng – Prof. of Lodz University of Technology

1. Legal basis for the review

The review was prepared on the basis of Resolution No. 58/7/IJK/2023 of the Council for Academic Degrees of the Lodz University of Technology in the disciplines: mechanical engineering, material engineering of July 10, 2023 on the appointment of a Doctoral Committee in the procedure for conferring a MSc. Eng. Cesar Israel Hernandez Vazquez with a doctoral degree (PhD) in the field of engineering and technical sciences in the discipline of material engineering.

2. Dissertation evaluation criteria

The assessment of the doctoral dissertation was based on four main criteria:

- ✓ the correct definition of the scientific problem and its topicality and originality;
- ✓ the correctness of research objectives and hypotheses and the level of their verification;

- ✓ correctness, consistency of the structure of the doctoral dissertation, presentation of research results and its inference;
- ✓ ability to independently conduct scientific work - workshop side.

3. The correctness of defining the scientific problem, its timeliness and originality.

The subject of the doctoral dissertation prepared by MSc. Eng. Cesar Israel Hernandez Vazquez is associated, among others, with the development of a procedure for the production of chitosan fibers by wet spinning with the use of carboxylic acids such as acetic, citric and lactic acids as a solvents, along with the determination of their properties. The study also examined the possibility of including ursolic acid as an antibacterial agent and tripolyphosphate as a cross-linking agent affecting the mechanical parameters of the fibers. It was important to prepare solutions of chitosan salts based on selected acids so that their form was as appropriate as possible in the wet spinning process.

In addition, the PhD candidate analyzed the rheological properties of a 7% solution of chitosan dissolved in citric and lactic acid. In the process of wet fiber production, the effect of polymer concentration on their parameters was also analyzed using sodium hydroxide as a coagulation medium. The author found that of the three mentioned solvents, acetic acid was the most suitable for solution preparation and fiber production by wet spinning. The experiments carried out and the analysis of the obtained results showed that the chitosan fibers produced from a 7% solution of chitosan in acetic acid have sufficient tensile strength and a smooth morphological surface. By absorbing ursolic acid on the surface of chitosan fibers, their antibacterial parameters were improved. The optimal mechanical strength of the fibers was obtained by cross-linking them with tripolyphosphate (TPP).

Fiber parameters were determined by FTIR spectroscopy, UV spectroscopy and tensile strength tests. The antibacterial activity was tested on *Staphylococcus aureus* and *Escherichia coli* strains. The obtained results showed that the strength of the fibers can be significantly increased by the use of the TPP cross-linking agent, and the antibacterial properties are increased by the ursolic acid absorbed on the surface.

The PhD student correctly identified the scope of research described above. He selected the materials and properly planned the research that was aimed to confirm and solve the defined scientific problem. Considering the current state of the art and the originality of the proposed solutions, it must be emphasized that chitosan and its modifications are a very popular topic and its use as a raw material in the wet spinning process is a natural solution. The application

potential of the polymer is very wide, its fiber-forming or antibacterial properties also seem to be crucial.

In the dissertation, the Author correctly defined the original research problem, the choice of which was supported by an analysis of the current state of knowledge in the field of material engineering, polymer chemistry, textiles (the bibliography is presented on 28 pages of the dissertation), the Candidate presented its universal solutions using the developed methodology using a number of instrumental methods.

4. The correctness of research objectives and hypotheses and the level of their verification.

With regard to the identified research problem based on an in-depth analysis of the literature, the PhD student presented a research thesis assuming that it is possible to produce fibers by wet spinning from chitosan solutions dissolved in carboxylic acids and their modification by cross-linking with tripolyphosphate (TPP) to improve mechanical and strength parameters, or improving their antibacterial activity by absorbing ursolic acid on the surface. In order to confirm the assumed research thesis, the author planned and conducted a series of experiments. With the research thesis presented in this way, the main goal of the doctoral dissertation was specified - to deepen the knowledge about the production of chitosan fibers by wet spinning in order to obtain better mechanical and antibacterial properties, as well as to study the impact of various carboxylic acids as solvents in the production process and their impact on the obtained fibers and their properties. Research also aimed to increase knowledge on how to improve the properties of chitosan fibers, which could lead to better biomedical materials for tissue engineering applications.

Additionally, attempts have been made to include a wider range of agents to improve antibacterial properties, which may be beneficial in preventing infection of implants and medical devices.

In the first stage, the Author produced fibers using the wet spinning technique, analyzing the effect of the type of solvent on their parameters, determining which one was the most convenient. In the next step, the PhD student analyzed the effect of chitosan mass concentration on the parameters of the spinning process and the quality of the fibers obtained. Next, he modified chitosan fibers by adsorbing ursolic acid on their surface to improve antibacterial activity. In the next stage, the PhD student subjected chitosan to chemical modification by

cross-linking it with tripolyphosphate (TPP), in order to improve the mechanical strength of the produced fibers.

The adopted structure of the doctoral dissertation is logical and allows for learning about the PhD student's thinking process. The proper implementation of the set goals along with the adopted research methodology allowed for a thorough analysis of the theses set out in the dissertation, as well as the achievement of the assumed goals. What is also worth emphasizing is the large number of experiments carried out and the wide spectrum of instrumental analyses used to explain the mechanisms affecting the change in the parameters of the produced fibers - in order to improve their antibacterial and mechanical properties. Presentation of research results, their analysis and explanations are a significant contribution to the development of materials engineering - especially in the field of practical applications in broadly understood biomedical engineering.

5. Correctness, consistency of the structure of the doctoral dissertation, presentation of research results and conclusions.

The layout of the dissertation is rather traditional (abstract, work motivation and aim, concepts, experimental research which presents the results of research obtained in successive stages, characterization of chitosan fibers, summary of findings and conclusions). The descriptions are generally correct, but there are repetitions and minor typos. In total, the dissertation has a volume of 124 pages, consists of 6 chapters, contains 41 figures, 27 tables and a list of bibliographies containing 74 items. The list of symbols, drawings, tables and literature facilitates the analysis of the dissertation. The sections of the PhD dissertation usually end with a summary and formulated partial conclusions. During the conducted research, the Author successively implemented the set main goal and specific objectives of the work and verified the main research thesis. As a result, he proved the legitimacy of the thesis, achieving the assumed goal - the implementation of basic research by conducting original experiments and chemical analyses. Using a number of research methods, the Author used measuring and analytical devices, such as: SEM scanning electron microscope, UV spectroscopy, total reflection infrared spectroscopy (FTIR), and a testing machine (ripper). The Author, summarizing the entire work, responsibly states that the work carried out is very complex and requires a broader view of the entirety of the problems.

The work has a correct structure, in which the chronology is justified and logical. From the formal point of view, it meets all the requirements by describing the discussed issues in detail.

6. Ability to independently conduct scientific work - workshop side.

Analysis of the content of the doctoral dissertation MSc. Eng. Cesar Israel Hernandez Vazquez allows us to conclude that the PhD student undertook an interesting research task and completed it to a degree that deserves full acceptance. A doctoral student with a fairly high research maturity systematically carried out the tasks he had set, consistently striving to achieve the desired goal. The author performed a number of laboratory and experimental works and chemical analyses and interpreted the obtained results.

As for any research aspect, it would be important to check the effect of the concentration of the solvent used on the parameters of the fiber production process and fiber properties.

It was impossible to find a clear answer in the work whether the attachment of ursolic acid is purely physical or chemisorptive?

There is also no explanation of how tripolyphosphate (TPP) cross-links, which groups react with TPP?

What is the antibacterial effect of fibers based on different solvents? – there is no comparison of these properties.

It would be interesting to explain the antibacterial mechanism - how chitosan and ursolic acid interact? - their synergy of action.

When determining the antibacterial parameters, there is no information whether chitosan fibers can only be bacteriostatic or are they bactericidal for the tested bacterial strains? – as is the case with fibers coated with ursolic acid.

Do the fibers also have fungicidal properties? – this aspect has not been addressed in the work, and due to the potential application, it seems to be inseparable.

Regardless of the above comments and questions, the workshop side of the thesis is correct, and the PhD student has demonstrated the ability to independently plan and implement the work.

7. Final conclusion - summary

Analyzing the entirety of the dissertation, despite the above-mentioned comments which the PhD Candidate can use in further scientific activity, it should be stated that the presented doctoral thesis meets the requirements for this type of scientific work. As a reviewer of the dissertation of Mr. MSc. Eng. Cesar Israel Hernandez Vazquez, I rate it positively. The presented analysis of the state of knowledge and the conducted experimental research show that

the work makes a significant contribution to the development of the research subject in question. The knowledge built in this way can be further used in the implementation of projects related to the development of new, innovative structures for biomedicine applications. The doctoral dissertation presents the Author's general theoretical knowledge also in disciplines related to the research subject and his ability to independently conduct scientific work. The subject of the doctoral thesis is an original solution to a scientific problem - optimization of methods for producing chitosan fibers by wet spinning and their modification in order to improve parameters. The Author found a gap in the widely analyzed and popular subject of chitin and its chitosan derivatives which he examined. The interdisciplinary nature of the work is also noteworthy. The doctoral dissertation is a written thesis in English with an abstract in Polish.

Therefore, I state that pursuant to Art.187. Act of July 20, 2018 - Law on Higher Education and Science, the reviewed doctoral dissertation by MSc. Eng. Cesar Israel Hernandez Vazquez meets the conditions set out in it. I also submit an application for the admission of Mr. MSc. Eng. Cesar Israel Hernandez Vazquez for further stages of the doctoral dissertation.



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