

Assoc. Prof. Anita Tarbuk, PhD  
(Senior Scientific Researcher in Technical Science/Textile Technology/Textile Chemistry)  
Vice-dean for Interinstitutional and International Cooperation  
University of Zagreb Faculty of Textile Technology  
Prilaz baruna Filipovića 28a, HR-10000 Zagreb  
Croatia

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### **Review report on Doctoral Dissertation**

**of MSc. Eng. César Israel Hernández Vázquez**

**entitled *Assessment of the effects of various carboxylic acids as solvents, characterization and enhancement of mechanical and antibacterial properties of wet-spun chitosan fibers***

(scientific supervisor Dr hab Inż. Zbigniew Draczyński)

prepared based on the invitation in accordance with Resolution no. 58/7/IIK/2023 of the Council for Academic Degrees of Lodz University of Technology dated July 10, 2023

The review was based on the English-language doctoral dissertation received from Lodz University of Technology. The dissertation consists of five chapters, including introduction, work motivation and aim, an overview of the state of the art related to the dissertation topic, concept of research based on biopolymers production and application, a presentation of the materials used in the research, namely chitosan, chitosan dope solutions, wet spinning and chitosan fiber, a presentation of scientific experimental results and a detailed analysis of the results, summary and conclusions, and a list of references. Also included are an abstract in English and Polish language, list of figures and list of tables. The dissertation contains 124 pages, 41 figures, 27 tables, and 74 references.

The first chapter "Work motivation and aim" presents the research problem, the aim and objectives of the dissertation, justification of the choice of the research study, and its scientific contribution.

The second chapter, "Concepts," reviews the current state of the problem and includes a review of the scientific literature. It includes information on biopolymer classification, production, and application in the medical industry related to biopolymer properties. Chitin and chitosan are covered in more detail, their preparation and activation with various carboxylic acids. The wet spinning process is also well explained. This work is supported by 52 references, 80% of which are scientific papers published in the last 10 years. In the third chapter, "Experimental Research," methods are presented and preliminary experiments with chitosan dopant solutions are explained in terms of their rheology. From the preliminary results, three samples were selected for further processing and characterization. The development of the wet-spun fibers with the composition of the batches and the parameters of the spinning process are presented in detail. The methods are supported by recent findings from the literature.

In the fourth chapter, "Characterization of chitosan fibers", experimental tests and the results obtained are presented clearly and in detail. First, the methods used for characterization are briefly explained, followed by the results obtained on the fibers. On wet-spun fibers were determined by scanning electron microscope (SEM), linear density and tensile strength. After surface modification of chitosan with tripolyphosphate (TPP), Fourier transform Infrared spectroscopy (FTIR) and UV spectroscopy were also performed. Antibacterial activity against Gram-positive bacteria, *S. aureus*, and Gram-negative bacteria,

*E. coli*, was determined by the standard method. The obtained results are commented, explained and compared with the results obtained by other researchers.

The fifth chapter "Summary of findings and conclusions", summarize the main findings and provides recommendations for future research.

The sixth chapter, "References", lists 74 sources, more than 60% of which are scientific papers published in the last 10 years. One paper has been published by the author of the dissertation. It should be noted that some references are not fully cited. Regardless of provided link or doi the full reference should be given.

In the dissertation, the author investigates the influence of various carboxylic acids as solvents for the production of chitosan fibers in the wet-spinning process. He explores the potential for improving the mechanical and antibacterial properties by surface modification of the wet-spun fibers. When comparing and evaluating the three carboxylic acids applied - acetic, citric and lactic acid, acetic acid with a concentration of 7% proved to be the most suitable solvent for the preparation of the spinning solution and the production of chitosan fibers, which have sufficient tensile strength and a smooth surface morphology. Furthermore, the incorporation of ursolic acid and tripolyphosphate (TPP) to improve chitosan fiber properties was investigated. Surface modification of chitosan fibers is possible by wet impregnation with ursolic acid solution, resulting in better antibacterial properties. When TPP is applied to the surface of chitosan fibers as a crosslinking agent, the mechanical properties improve. These results represent a valuable contribution in the field of chitosan fibers and their potential applications in industry, especially in the medical field. The dissertation fully corresponds to the problems of the field of materials engineering. The scientific work presents original results in a clear and logical presentation and meets the requirements for a dissertation. The conclusions are based on the research results.

## Questions and remarks

### Remarks.

- When reading the dissertation, one can assume the hypotheses of this work. It would be much better if they were clearly formulated and stated.
- There are far too many subheadings. It is not advisable to divide a chapter into smaller parts if the subchapters are extremely short, some have only 1 sentence. In my opinion, such short chapters can be merged or more information can be given about the subtopic.
- The methods are listed immediately before the results and the result is given. In the results, some statistical parameters are given. In the methodology, only the machines are given without any statistics. It would be better if the methods were listed in the experimental section with statistic parameters, and only the results and discussion in the results section.
- Regarding the references, it should be noted that they are not fully cited – in many cases the authors are missing, e.g. [8] Leticia P. Amenorfe, Eric S. Agorku, Frederick Sarpong, Ray B. Voegborlo, Innovative exploration of additive incorporated biopolymer-based composites, Scientific African, Volume 17, 2022, e01359, ISSN 2468-2276, <https://doi.org/10.1016/j.sciaf.2022.e01359>.  
[23] Sayari N, Sila A, Abdelmalek BE, Abdallah RB, Ellouz-Chaabouni S, Bougatef A, Balti R. Chitin and chitosan from the Norway lobster by-products: Antimicrobial and anti-proliferative activities. Int J Biol Macromol. 2016 Jun;87:163-71. doi: 10.1016/j.ijbiomac.2016.02.057. Epub 2016 Feb 24.

PMID: 26920243.

- [51] Baglin I, Mitaine-Offer AC, Nour M, Tan K, Cavé C, Lacaille-Dubois MA. A review of natural and modified betulinic, ursolic and echinocystic acid derivatives as potential antitumor and anti-HIV agents. *Mini Rev Med Chem*. 2003 Sep;3(6):525-39. doi: 10.2174/1389557033487917. PMID: 12871156.
- [52] Kashiwada Y, Wang HK, Nagao T, Kitanaka S, Yasuda I, Fujioka T, Yamagishi T, Cosentino LM, Kozuka M, Okabe H, Ikeshiro Y, Hu CQ, Yeh E, Lee KH. Anti-AIDS agents. 30. Anti-HIV activity of oleanolic acid, pomolic acid, and structurally related triterpenoids. *J Nat Prod*. 1998 Sep;61(9):1090-5. doi: 10.1021/np9800710. PMID: 9748372.
- [53] author is CI Hernandez Vazquez – this reference can not be found
- [61] *Handbook of Nonwoven Filter Media*, 1st Edition - February 13, 2007, Author: Irwin M. Hutten, eBook ISBN: 9780080471587
- [62] *Comprehensive Composite Materials II*, 2nd Edition - August 3, 2017, Editors: Carl H. Zweben, Peter Beaumont, ISBN: 9780081005330
- [63] *Yarn Count in Direct System and Indirect System*, October 30, 2015 by Mahedi Hasan  
.... Regardless of provided link or doi the full reference should be given.
- The CV and the bibliography of the doctoral student are not given, it would be nice if they were included in the dissertation.

#### **Questions.**

1. In the results, some statistical parameters are given. *What statistical analysis methods were used to analyse and evaluate the results obtained? How many elementary tests were performed to obtain one experimental point?*
2. Tests for *S. aureus* and *E. coli* were performed as they are the most common bacteria on textile. Chitosan also has an effect on microfungi. *Can it also be tested for Candida or Aspergillus, which are very common on textiles?*
3. *What would be the application for this material?*
4. *Now it is for a one-time application. Do you think it is possible to make chitosan fibres that are washable and reusable?*

#### **Conclusion:**

The submitted dissertation meets all formal requirements of Article 187 of the Law on Higher Education and Science of July 20, 2018 and complies with the principles and requirements for the structure of scientific research. In my opinion, the dissertation presented by César I. Hernández Vázquez submitted dissertation is ready to be defended orally before the competent committee. Therefore, I recommend the dissertation for the next procedure at the Lodz University of Technology. In case of a positive result of the dissertation defence, I recommend that César I. Hernández Vázquez the doctoral degree (Ph.D.).

