OPINION

by Prof. Dr. Tsvetanka Babeva
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regarding a dissertation submitted for the award of the educational and scientific degree "Doctor" in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.1 Physical Sciences, doctoral program "Electrical, magnetic and optical properties of condensed matter".

Author: Alexander Vasilev Grigorov

Dissertation title: Modified multilayer structures for immobilization of bioactive molecules

Scientific supervisor: Assoc. Prof. Dr. Asya Viraneva

1. General presentation of the procedure and the doctoral candidate

The set of materials submitted electronically by the doctoral candidate Alexander Grigorov includes the following documents: an application to the Rector of Plovdiv University for opening the procedure, a CV in Europass format, a protocol from the departmental council for preliminary discussion of the dissertation, an opinion by Assoc. Prof. Viraneva for opening the defense procedure, an abstract in Bulgarian and English, a declaration of originality and authenticity of the submitted documents, a report on meeting the minimum and additional requirements of Plovdiv University, a list of scientific publications, the dissertation manuscript, and copies of four publications related to the dissertation. All submitted documents fully comply with the Regulations for the Development of the Academic Staff of Plovdiv University (Art. 36, para. 1).

Alexander Grigorov obtained his Bachelor's degree in 2015 from the University of Aberdeen, United Kingdom, and in 2018 graduated with a Master's degree in professional field 4.1 Physical Sciences from Plovdiv University "Paisii Hilendarski". In 2019, he was enrolled as a full-time doctoral student. He is currently an Assistant Professor in the Department of Physics at the Faculty of Physics and Technology of Plovdiv University, where he carries out teaching and research activities. He is a co-author of 37 publications indexed in Scopus, which have received 59 citations. His *h*-index is 4. He has participated in the research teams of six scientific research projects.

2. Relevance of the research topic

The thesis under review aims at the development of polyelectrolyte multilayer films deposited on modified substrates of polylactic acid and poly(ε-caprolactone) and their application as drug delivery systems. Research on materials and systems for controlled drug release is extremely relevant, as it provides opportunities for significantly improving the efficacy and safety

of therapies, reducing side effects, and has the potential to revolutionize the treatment of various diseases, including chronic, oncological, and infectious conditions.

3. Knowledge of the research problem

The literature review in the dissertation is characterized by clarity of presentation combined with a high scientific level and the use of appropriate terminology. The research problem is formulated clearly and unambiguously, and the existing solutions to date are reviewed and systematized. A thorough and critical analysis of the state of the art is carried out, based on an extensive review of more than 200 literature sources, most of which are from recent years. As a result, the scientific niche motivating the formulation of the objectives and tasks of the dissertation is clearly identified. This demonstrates both in-depth knowledge of the research problem and well-developed analytical skills and abilities for critical assessment, interpretation, and synthesis of a large body of scientific information.

4. Research methodology

To achieve the goals, polylactic acid (PLA) and poly(ε-caprolactone) (PEC) were selected as substrates for polyelectrolyte multilayer systems (chitosan, xanthan, and casein), in which biologically active substances such as β-galactosidase, curcumin, benzydamine hydrochloride, and tolfenamic acid were immobilized. All materials are described in detail in Section IV "Materials and Methods" of the dissertation, including a critical analysis of their advantages, disadvantages, and application areas. The same section describes the preparation and characterization methods. Substrates of PLA and PEC were obtained using the gravitational casting method ("solution casting"), and multilayer polyelectrolyte systems were deposited by the "dip coating" technique. Structural and property modifications were achieved using chemical treatments, lyophilization, and corona discharge treatment. The properties of the deposited samples were studied by DSC (Differential Scanning Calorimetry), SEM (Scanning Electron Microscopy), and contact angle and surface energy measurements. The methods used to determine the immobilization efficiency and release behavior of the studied enzyme are also described clearly and in detail. Overall, the applied research methodology is appropriate and leads to solving the stated tasks and achieving the research objectives.

5. Characteristics and evaluation of the dissertation and contributions

The dissertation is written on 164 pages and includes an introduction, three chapters, conclusions, contributions, and references. The introduction presents concisely the problems related to controlled delivery of bioactive substances, the materials used, and the adopted approach. This is followed by a literature review that discusses in detail the materials and methods for producing multilayer biopolymer structures, their modification, the immobilization of bioactive substances, and their controlled release. Based on the literature review, the objectives and tasks of the dissertation are defined.

The experimental results are presented in two chapters—one describing the materials and

methods, and the other the results and discussion. The presence of summaries at the end of each subsection makes a very good impression. The results are clearly illustrated with appropriate figures and tables. The conclusions are well summarized within one and a half pages.

The doctoral candidate has defined six contributions of the dissertation. These contributions are of a pure scientific and applied scientific nature, mainly related to demonstrating, by novel experimental approaches, essential new aspects of existing scientific problems in the field of polyelectrolyte multilayer systems and biodegradable polymer carriers. They include the acquisition and proof of new scientific facts concerning the influence of electric fields, various surface modifications, and the porous structure of polylactic acid and poly(ε-caprolactone) substrates on immobilization, enzyme activity, and the kinetics of controlled release of bioactive substances from polyelectrolyte multilayer structures.

6. Evaluation of publications and the doctoral candidate's personal contribution

The results of the dissertation are summarized in four publications published in the journals Coatings (2 papers), classified as Q2, Bulgarian Chemical Communications (Q4), and Journal of Chemical Technology and Metallurgy (Q3). All three journals are indexed in Scopus, but only the first two are also indexed in Web of Science (i.e., have an impact factor). The doctoral candidate is the first and corresponding author of one of the papers.

I do not know the doctoral candidate personally and therefore cannot assess his personal contribution based on direct observations; however, after reviewing the dissertation, abstract, and all submitted materials, I consider his personal contribution to the obtained results to be substantial.

7. Dissertation abstract

The dissertation abstract is written in Bulgarian and English, has a length of 32 pages, and reflects the main results and contributions of the dissertation.

8. Critical remarks and recommendations

I have the following critical remarks, which do not affect my overall positive assessment of the dissertation:

1. On page 90 of the dissertation, it is stated that "*the formation of pores in PLA, PEC, and their composite films leads to an increase in the degree of crystallinity*." Table 4 shows that this is valid only for PLA and the 50/50 composite with PEG and is not valid for the lyophilized samples and PEC.

2. Experimental errors of the measured quantities are missing, making it difficult for the reader to assess whether the observed changes are significant or within the margin of error.

3. Some figures in the dissertation are unnecessary. For example, Figure 32 summarizes Figures 29, 30, and 31, and Figure 36 summarizes Figures 33, 34, and 35.

CONCLUSION

The dissertation contains fundamental and applied scientific results that represent an original contribution to science and meet all requirements of the Act on the Development of the Academic Staff in the Republic of Bulgaria, its implementing regulations, and the relevant regulations of Plovdiv University "Paisii Hilendarski". The dissertation demonstrates that the doctoral candidate Alexander Grigorov possesses in-depth knowledge and professional skills in the scientific specialty "Electrical, Magnetic and Optical Properties of Condensed Matter", and shows the ability to conduct independent scientific research. Based on the above, I confidently give my **positive evaluation** of the presented dissertation, abstract, results, and contributions, and **propose that the esteemed scientific jury award the educational and scientific degree "Doctor" to Alexander Vasilev Grigorov** in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.1 Physical Sciences, doctoral program "Electrical, Magnetic and Optical Properties of Condensed Matter."

February 12th 2026

Prepared by: .....

Prof. Dr. Tsvetanka Babeva