

## REVIEW

by

Prof. Dr. Elena Vassileva

Member of the Academic Jury set to render a decision on a procedure for the acquisition of Academic Degree “Doctor of Philosophy” (PhD) in the Professional Field **4.2. Chemical Sciences** according to the Classifier of the Areas of Higher Education and the Professional Fields (Scientific Specialty “Polymers and Polymer Materials”)

This Peer Review is prepared following the decision made by the Academic Jury in response to Order № ПД 09-182 from 02.12.2025 issued by the Director of the Institute of Polymers, Bulgarian Academy of Sciences. The Review is in compliance with *Development of Academic Staff in the Republic of Bulgaria Act (DASRB)*, *the Rules for the Application of the Development of Academic Staff in the Republic of Bulgaria Act*, *the Rules of BAS* and with *the Rules set at the Institute of Polymers, Bulgarian Academy of Sciences, for applying the Act aforementioned.*

*PhD candidate:* Ina Anastasova

*Title of dissertation:* Electrospun Hybrid Materials from Poly(l-lactide-co-d,l-lactide) and Chitosan Derivatives with Directedly Modeled Design for Potential Applications in Biomedicine and for Photocatalytic Water Purification

*Scientific Supervisors:* Prof. Dr. Olya Stoilova

Prof. Dr. Milena Ignatova

The dissertation of Ina Anastasova is fully in line with the trends of the advanced polymer science, combining scientific research of both fundamental and applied nature which is important for the fields of medicine and ecology. The division of the dissertation in two different chapters each one focused on separate application field does not affect the integrity, but demonstrates the diverse applications that polymer materials obtained through electrospinning could have.

The literature survey, written on 42 pages, presents chitosan and poly(lactic acid) as widely used polymers in practice and justifies their choice as the main components of the materials developed in the dissertation. The antibacterial activity of chitosan and its derivatives, as well as the biodegradability of poly(lactic acid), is described, i.e. their most important advantages in terms of target applications are appropriately outlined. The method for obtaining the materials, namely electrospinning, is well presented, and the parameters that influence the morphology and properties of the polymer fibers are analytically described. The literature review concludes with a presentation of electrospun fibers based on chitosan and poly(lactic acid) developed to date and reported in the literature, as well as hybrid ones, for example, obtained with the inclusion of TiO<sub>2</sub> and ZnO nanoparticles.

The experimental part of the dissertation, described on 10 pages, is presented clearly and concisely, describing the specific procedures for the synthesis of the bioactive and catalytically active components, as well as the conditions under which the fibrous materials were obtained. The methods for characterizing the obtained materials are selected appropriately and provide complete information about their structure and properties.

The results obtained within the dissertation are presented on 37 pages. Chapter 1 of the dissertation describes the preparation, characterization and application as biomaterials of fibrous materials from PLDLLA and the newly synthesized Schiff base of chitosan with 8-hydroxyquinoline-2-carboxaldehyde. They are additionally functionalized by complexation with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions in order to enhance their biological activity. The main contribution of this study is in the development of fibrous materials from PLDLLA/Ch-8Q and their complexes with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , which exhibit high antitumor activity against HeLa and MCF-7 cells, while maintaining lower toxicity against non-cancerous BALB/c 3T3 fibroblasts.

Chapter 2 of the dissertation presents the preparation, characterization and application of hybrid electrospun materials from PLDLLA,  $\text{Fe}_3\text{O}_4$  and ZnO nanoparticles. Different architectures were used, with the addition of quaternized N,N,N-trimethyl chitosan iodide (QCOS) as an adhesion agent for ZnO nanoparticles located on the surface of the fibers. The antioxidant activity of the developed materials was shown, and it was significant for ZnO and QCOS containing mats. It was shown that ZnO nanoparticles impart significant photocatalytic activity, demonstrating stability in five consecutive cycles of UV irradiation. The mats exhibit magnetic properties due to  $\text{Fe}_3\text{O}_4$  nanoparticles, which allows their easy separation from the treated wastewater. Thus, the study results into the development of materials with very good potential as membranes for water purification, as they allow for the effective removal of organic pollutants and dyes by heterogeneous photocatalysis.

Below are provided recommendations related mainly to the way of presenting scientific information:

1. The expression “glassy transition” is incorrect, “glass transition” should be used
2. In Figure 12, it would be good to present the DSC curves for chitosan and 8-hydroxyquinoline.
3. A scheme presenting the complexation of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  by the fibrous materials from PLDLLA/Ch-8Q would be useful.

The lack of spelling errors is really impressive.

*Questions:*

1. Do you have an explanation for the observed decrease in the dynamic viscosity of the PLDLLA spinning solutions upon addition of chitosan, as well as upon inclusion of the Schiff base Ch-8Q. Why does the spinning solution used to obtain PLDLLA/Ch-8Q 50:50 have the lowest viscosity?
2. Has the quantitative determination of the complexing agents ( $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions) in the PLDLLA/Ch-8Q mats been made or has there been an attempt to optimize the content of these ions in the mats?
3. Have stability tests been performed on the obtained hybrid mats based on PLDLLA,  $\text{Fe}_3\text{O}_4$  and ZnO, with a view to potential leaching of the nanoparticles included in them?

The presented scientific research is innovative, with a clearly defined ultimate goal, namely the creation of materials with biological activity (Part 1) and with environmentally oriented application (Part 2). The design of both types of materials and the selected

characterization methods are logical, well-planned, and the sequence of steps is well-founded and follows logically from the set goals. The selected synthesis and characterization methods are appropriate and fully in line with the final goal of the study. The presentation of the obtained data and the described discussion of the obtained data show in-depth thinking and precise work of the PhD student and her supervisors. The observed trends in both types of newly developed materials are correctly outlined, and they are clearly and correctly explained. The results obtained from the presented studies support the set goal and show the appropriateness of the chosen approach. The dissertation demonstrates the PhD student's ability to plan and conduct scientific research, while at the same time correctly reflecting the observed trends and providing a correct interpretation of the obtained results.

The dissertation fully meets the specific requirements of the Institute of Polymers, Bulgarian Academy of Sciences, namely:

- contains fundamental and applied scientific results that represent an original contribution to the field of polymer science and related applications
- has the type and volume corresponding to the requirements in the field of advanced polymer research
- presents results included in two scientific publications (in the journal *Polymers*), for which 14 citations have been noted so far. The selected journal in which the results were published has a high impact factor (4.9 and 5 in the different years, respectively) and is in the Q1 quartile.

According on the grounds of the documentation presented by the candidate, on her publications reviewed and the above assessment, I recommend on the Academic Jury to render a positive decision for the acquisition of the Academic Degree PhD on Ina Anastasova.

Reviewer: .....

Prof. E. Vassileva

Member of the Academic Jury

Sofia, 09.02.2026