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Review report on the doctoral dissertation

of MSc Sima Shakoorjavan

entitled: "**Layer-by-layer deposition of PAMAM dendric material onto polylactide nonwoven**"

Dissertation supervisor: ***Prof. DSc. Eng. Dawid Stawski, TUL, Poland***
Dr Somaye Akbari, AUT, Iran

The review was prepared in a response on the letter from Prof. Katarzyna Grabowska, vice-Chair of the Disciplinary Council of Materials Engineering of the Lodz University of Technology, dated December 3, 2024.

As required by the Law on Higher Education and Science with art. 187 of the Act of 20 July 2018 (Journal of Laws 2018, item 1668, as amended) the dissertation review contains the following elements:

- evaluation whether the doctoral dissertation represents an original solution to a scientific problem;
- an assessment whether the doctoral dissertation presents the general theoretical knowledge of the applicant for the to be awarded a doctoral degree;
- an assessment whether the doctoral thesis demonstrate the ability of the applicant for the doctoral degree to carry out independent scientific work.

Scientific value and topicality of the dissertation

MSc Sima Shakoorjavan in her doctoral thesis dealt with the issues related to the modification of nonwoven with the use of polyelectrolytes via the layer-by-layer method. This work is in line with the global trends of functionalizing materials with various chemical compounds in order to endow them with new properties. Currently, in many research teams intensive work is being carried out on the possibility of improving the drug delivery systems. In the literature there are many scientific studies related to various types of modifications of nonwovens. There are still many research problems to be solved. Polyelectrolytes applied on polylactide (PLA) nonwovens via the layer-by-layer technique is a scientific advancement, which opening new possibilities of employing this type of textile materials. Polymeric dendrimers are a group of polymers that currently arouse great interest regarding their applicability not only in medicine but in electroplating processes, catalytic systems and in manufacturing various sensors. The concept of the discussed PhD dissertation was to obtain nonwoven fabrics modified with the poly(amidoamine) dendrimer (PAMAM) and poly(acrylic acid) (PAA). In the theoretical part, the PhD student presented the characteristic and possibilities of using polymeric dendrimers in various types of applications. This part of the work also includes information on polymer modification, referring to the latest literature reports. MSc Sima Shakoorjavan presented the research aimed at developing optimal conditions for the modification of polylactide nonwoven materials with polyamine dendrimers and poly(acrylic acid). The conditions for pre-treating nonwoven fabrics via the aminolysis reaction in different time intervals and at different temperatures were examined thoroughly. It was possible to determine the highest content of amine groups on the was tested nonwovens, which had an impact on the realization of the layer-by-layer process. As a result of thorough testing, the PhD student assessed the changes in the chemical structure and properties of the polyelectrolytes modified nonwovens. The dissertation topic is current and relevant in the materials engineering. The MSc Sima Shakoorjavan selected an original and important research problem leading to developments in science. Due to the properly selected research methodology and the obtained results, the multilayers nonwoven materials were manufactured and evaluated. The results presented in the doctoral dissertation advance knowledge in the field of materials engineering, especially with regard to nonwoven materials modifications via the layer-by-layer method.

Evaluation of the research theses and the work aim

The PhD student presented the aim of her dissertation, which was to examine the structure of the multilayer systems consisting of poly(amidoamine) - dendrimers and poly(acrylic acid). The systems were applied on a pre-modified polylactide nonwoven fabric using the layer-by-layer technique. MSc Sima Shakoorjavan presented seven research theses in her dissertation. The aim and research theses are described in detail. The thesis present many experiments and results with comments and analysis. In my opinion the aim and research hypotheses were formulated correctly. The work scope consisted in:

- the modification surface structure of PLA nonwovens by optimizing the aminolysis process;
- optimizing the process of obtaining a polyelectrolyte complex (i.e. studying pH and concentrations of PAMAM and PAA);
- analysing the polyelectrolyte layers formation in the layer-by-layer process;
- evaluating the chemical structure and properties of multilayers PLA nonwovens.

I positively evaluate this doctoral dissertation regarding the objective and the theses. The scope of research proposed by the PhD student was appropriate, as it verified the research hypotheses and the assumed goal of the work was achieved. All experimental methods have been described clearly and in detail. In my opinion, the methodology was adequate to the research problem. The conducted studies provide a solid foundation for fundamental and applied research.

Assessment of the research results presentation

The dissertation form contains 121 pages, including 7 schemes, 24 figures and 15 tables. The work is divided into two main parts: a theoretical part and an experimental part with conclusions. Additionally, the doctoral thesis includes: an abstract, introduction, supplementary data section, references, a list of abbreviations, and a list of figures, schemes and tables. The theoretical part begins from chapter 1 with the introduction and presentation of the research hypotheses. Chapter 2, authored by Ms' Sima Shakoorjavan in the literature review, presents information on polymer modifications. In the case of polymer modifications, the classification includes polymer blending technique, grafting and curing. The author also indicates the possibilities of modification both in bulk and on the surface. For surface modification, the grafting, aminolysis and layer-by-layer method is presented. The modifications used in this work (layer-by-layer and aminolysis) are described in more detail. The PhD student discusses issues related to various mechanisms of multilayers assemblies deposited on the substrate via

the layer-by-layer (LBL) technique, governed by several key factors, such as: polyelectrolyte pH, ionic strength, polyelectrolyte concentration, intermediate drying, adsorption time, intermediate rinsing. In my opinion, there is a need for a more appropriate arrangement of subchapters, it would be better to place the problems regarding polyelectrolytes before section of the layer-by-layer methods. Chapter 2.3 of the dissertation is devoted to dendritic polymers, presenting their synthesis, structure, properties and applications. In the next two brief chapters, there is information on the research object, which is polylactide (PLA). The author incorrectly numbered the chapters in this part of her work (chapter 2.3 – Dentritic Polymer). Polylactide (PLA) is the main research object and should be described in more detail, for example: its production process, modifications, properties. The chapter 2.4 is devoted to nonwoven technology. Similarly to the chapter on PLA, the PhD student described this topic in a very general manner. It would be more reasonable to focus on the spun laid technology which was used to obtain the research object. Chapter 3 is a presentation of the main objective and the work scope. The experimental part (chapter 4), subchapters 4.1 and 4.2 focus on the materials and the research methods used in the further part of the work. Critical comments of this section is a too general characteristics of the nonwovens. The doctoral student should provide us with more detailed information in this regard. Moreover, the author does not explain why this particular method of forming nonwovens was selected for the research. In general, PLA-based nonwovens (e.g. needle-punched or obtained by electrospinning) are usually considered as carriers of biomaterials or drug delivery systems. MSc Sima Shakoorjavan should have explained the reasons for choosing this type of the nonwovens and provide us with more information for choosing the aminolysis and layer-by-layer parameters (e.g. pH, temperature process, time and polyelectrolytes concentration). In the fifth chapter "Results and discussion", subchapter 5.1 contains the result of experiments and analysis of the PLA materials pre-modification (aminolysis process). Figures and tables are correct and support the analysis of the results. Only the SEM+EDS (Figure 7) is of poor quality and should be improved. PhD student in section 5.2 designed and obtained the polylactide nonwoven with PAMAM/PAA multilayer assemblies on the pre-treatment nonwovens with optimized conditions obtained previously. The author presents the pH effect and the concentration ratio of polyelectrolyte on the formation of multilayers PAMAM/PAA in subchapter 5.2.1.2 and subchapter 5.2.1.3. The next chapter presents how important it is to create optimal procedures of forming polymer compositions. The analysis of changes in the liquid-liquid system led to the proper selection of the optimal process conditions for the liquid-solid system. The Author was analysed: the effect of polyelectrolyte concentration on multilayer growth, FTIR-ATR, growth profile

of multilayer systems on nonwovens. In chapter 5.2.2.4, the MSc Sima Shakoorjavan also analyses the effect of intermediate drying on the growth profile. The conducted tests revealed different behaviours on the forming multilayers on PLA nonwovens, depending on type of polyelectrolyte. In this part PhD student analyses the dried process of nonwoven, and compared to the undried ones. MSc Sima Shakoorjavan proposes two possible hypotheses, which demonstrates her ability to conduct a scientific discussion. Last chapter 6 of the dissertation, PhD student presents the four conclusions regarding to: the aminolysis process of polylactide nonwoven; characterization and optimization of polyelectrolyte complex formation in liquid-liquid phase; obtaining multilayer assemblies on pre-treated PLA in liquid-solid phase; structural confirmation and properties analysis of polyelectrolyte multilayers.

The doctoral thesis presents original results, which are clearly presented. Nevertheless, in this work we find editorial errors, incorrect chapter numbering, poor quality figure and incomplete information regarding the results. For example, Figure 7 (SEM+EDX analysis) is no information whether it is a point analysis or a map of the area. Simultaneously, it would be better to change some nomenclature of sample e.g. "neat PLA" to "non-modified PLA". The list of the used abbreviations have an incorrect definition of "PLA1" and "PLA2". Moreover, using the "PE" of abbreviations is inappropriate, because this acronym is very often used to refer to polyethylene in scientific manuscripts. Another comment concerns the notation of abbreviations immediately following each other e.g. "PAMAM PE", "PAA PE".

Summarizing, I rate the dissertation as good in terms of its scope. The topic of the dissertation corresponds to the problems of the field materials engineering. The scientific thesis is supported by literature studies. The references include over 160 items. The research results are presented in an appropriate manner, the described relationships are clearly and logically illustrate. Based on the content all parts of the dissertation, I state that MSc Sima Shakoorjavan has proved her knowledge topic of layer-by-layer materials modification, ability to plan the research, prepare experiment, and correctly interpret the obtained results.

Comments and questions for the PhD student

A list of comments, observations, questions about the dissertation that the doctoral student should explain:

- The material selection. What was the basis for using the spun-laid of PLA nonwovens with the parameters of 40 g/m^2 and 120 g/m^2? There is no detailed description of the nonwoven manufacturing. How did the structure of nonwoven affect the modification process? Please explain the influence of fibres diameter, nonwoven porosity.

- Author presented the conditions of the aminolysis process but there is no comment on the applied process temperatures and adopted time intervals.
- Did the PLA glass transition temperature influence the amine group density obtained on the nonwoven fabric surface?
- The water contact angle results for PLA1 and PLA2 nonwovens are presented for one particular temperature of the aminolysis process. Did differences also occur at room temperature?
- Why didn't the author present the hydrodynamic radii values for PAMAM and PAA at the same pH values?
- The layer-by-layer process was conducted in order to obtain 8 layers. Was the experiment conducted to apply for more layers number?
- The author should indicate the acceptable levels of mechanical properties of modified PLA nonwovens.
- Did the author determine the growth inhibition zone in microbiological test?

Final conclusion

PhD student demonstrated knowledge of the study and analysis of modified polylactide nonwovens by layer-by-layer methods. The analysis of the content presented in dissertation is statement that the PhD student specified the research problem in an appropriate manner, demonstrated the ability to independently conduct scientific research and has the necessary theoretical knowledge in the field of materials engineering. The doctoral thesis of MSc Sima Shakoorjavan is an original scientific and research work and relevant on the development material engineering. The comments and observations presented in the review report do not detract its scientific and cognitive value of the dissertation. In my opinion the reviewed dissertation entitled "Layer-by-layer deposition of PAMAM dendric material onto polylactide nonwoven", prepared by MSc Sima Shakoorjavan meets the requirements for doctoral dissertations in accordance with art. 187 of the Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended) in the scientific discipline of **materials engineering. Therefore I request to the Disciplinary Council of Materials Engineering of the Lodz University of Technology that MSc Sima Shakoorjavan be admitted to the further stages of the doctoral procedure.**