R E V I E W
by

Assoc. Prof. Filip Ublekov, PhD
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 in response to Order № РД-09-178 of 19.12.2024

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*.

1. Biographical information about the candidate

Simona Zahova graduated from the University of Chemical Technology and Metallurgy in Sofia in 2015, where she obtained a Master's degree in the field of polymers. During her studies, she started working at CRV Globar Ltd., as a trader of polymers, additives and masterbatches. In 2017, he held the position of Sales Manager at Impextim Ltd. The company's activities include the supply, trade and distribution of polymers, elastomers, masterbatches, industrial chemicals and yarns for the textile industry. Simona Zahova has been enrolled for full-time doctoral studies as of 01.01.2019 in the scientific specialty "Polymers and Polymeric Materials" in the scientific field "Polymers for Alternative Energy and Environmental Protection" at the Institute of Polymers-BAS with scientific supervisor Assoc. Prof. Violeta Mitova, PhD and scientific consultant Prof. Kolyo Troev, PhD. Simona Zahova has submitted all the necessary documents in accordance with the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (RASRB), the Regulations for its implementation, and the relevant Regulations of the Bulgarian Academy of Sciences and the IP-BAS.

2. Assessment of the scientific and research accomplishments of the candidate

The aspiration of modern society for sustainable development, environmental protection and successful waste management poses several challenges to society. The purpose of the dissertation is closely related to the recycling of the most produced industrial polymer - PET and the subsequent use of its degradation products in accordance with the adopted European directives. The dissertation is written on 118 pages and contains 37 figures, 8 tables and 10 schemes. 306 literary sources were used, most of them in the last 10 years. The dissertation consists of 7 separate sections, namely: Literature review, Experimental part, Results and discussion, Conclusions, Offerings, Application and References. The Literature Review is well structured and gives a very detailed and accurate idea about the topic of the dissertation. Extremely detailed in the Literature Review examines the importance of the use of PET, as well as strategies for managing PET waste and possible methods for its recycling and degradation. The literature review concludes with generalized conclusions, which lead to the thesis that the glycolysis process effectively breaks down PET into BHET and oligomers. The end products of degradation can be used for the synthesis of PET, as well as to produce other polymers with high added value. The most used catalysts in this process have some disadvantages - organic activity and selectivity, negative environmental impact and high cost. On this basis, two main objectives

of the dissertation are formulated, namely, to synthesize and characterize an effective catalyst for conducting PET glycolysis and determining the optimal conditions for the process. The second objective relates to the preparation and characterization of phosphorus-containing compounds based on PET glycolysis products with potential applications as fire retardants. To solve it, 4 main tasks have been identified, which are logical and determine the development of sustainable environmentally friendly materials and processes in the context of the development of a green economy. In the experimental part the materials used, the preparation of the used titanium (IV)phosphate catalyst, the glycolysis of waste PET with and without the presence of a catalyst during conventional and microwave heating, the determination of the amount of BHET in the degradation product, as well as the interactions of the degradation products of PET with DHFFC and TMF are systematically and thoroughly presented. Back to section Results and discussion The synthesized titanium (IV) phosphate, the obtained monomers from the glycolysis of PET, as well as the phosphorus-containing products based on waste PET have been analyzed in detail through various instrumental methods. A comparison and analysis of the influence of reaction conditions in the process of smoothing PET under conventional and microwave heating is made. It has been demonstrated that the use of microwave heating in PET glycolysis has been shown to reduce the time for depolymerization. It was found that when using only 0.2 wt. % of the synthesized titanium (IV) phosphate catalyst, the degradation time is reduced by 12 times compared to that of conventional heating and without the use of a catalyst. In accordance with the concept of "green chemistry", the reaction was carried out with minimal use of solvent at a mole ratio of PET:EG = 1:2.77. The resulting degradation products from BHET are a well-defined mixture of monomers, dimers and trimers and other oligomers. The second goal of the dissertation is related to the preparation and characterization of phosphorus-containing compounds on the basis of obtained products of PET glycolysis, which is discussed in the last two subparagraphs of the section. The interactions and possible reactions of the resulting mixture of PET glycolysis with DHFFC and TMF have been studied. The structure of the resulting oligomeric products is determined. The thermogravimetric analyses of the resulting products show the presence of a charred residue between 13 and 17 %, which confirms their potential application as fire retardants.

3. Assessment of the qualities of the extended abstract of the doctoral thesis, whether it correctly reflects the contributions of the doctoral thesis

The abstract contains the necessary sections and fully corresponds to the content of the dissertation in terms of the research carried out, the results obtained, and the conclusions made. The main contributions of the dissertation have scientific and applied orientation and can be related to the development of more promising and "green" methods for degradation of PET through microwave exposure and the presence of a more environmentally friendly catalyst than titanium (IV)phosphate. Methods for increasing the value of the resulting degradation products from PET glycolysis with DHFFC and TMF are described.

4. Opinions, notes and recommendations

The results of the scientific research included in the dissertation of Simona Zahova have been published in two international specialized scientific journals with a high impact factor (4.2 and 5.9), which fall under Q1. A total of 9 citations according to Scopus (without auto-citations) have been noticed in the publications. Simona Zahova is the first author in both publications, which undoubtedly confirms his contribution to the experimental work and the shaping of scientific results. The results of the dissertation have been reported at 7 scientific forums. The proposed development "Glycolysis of waste PET under conventional and microwave heating" has been selected as the most significant scientific and applied achievement of IP-BAS for 2023. Based on the above, I believe that as a result of the research, the PhD student Simona Zahova has

acquired knowledge, skills and ability to correctly interpret the results obtained using modern methods of synthesis and analysis. Critical remarks and comments.

I have the following remarks and questions about the dissertation:

1. The literature review is too extensive and detailed. It covers almost half of the volume of the dissertation - 46 out of a total of 118 pages. I believe that the length of the text in this section can be shortened.

2. The use of different units of measurement for the physical quantity of pressure makes an unpleasant impression. In some places it is noted in atm., MPa or bar, which makes it difficult to compare under the reaction conditions of different processes.

3. In the Results and Discussion section on page 70, it is concluded that based on calculations of the power of the heat sources used – a magnetic stirrer (600W) and a microwave reactor (450W), energy savings of approximately 22% were achieved. In my opinion, this conclusion is incorrect, and such a statement would be valid if it were made on the basis of actual electricity consumption.

4. Pages 56 and 57 list the apparatus and methods used. The equipment is described quite briefly, as well as the corresponding methods. In my opinion, this is a major disadvantage of the dissertation.

5. On page 16 it is described that most manufacturers of recycled PET materials operate under drying conditions in the range of 140 °C – 170 °C. On page 14 in subsection 3.1.2 Water as a contaminant, it is noted that such "contamination" by moisture should be less than 0.02%. In Section II Experimental Part on page 48 it is written that for the purposes of the experiment PET flakes of uniform size were selected, which were dried for 12 hours at a temperature of 80°C. My question is related to whether this condition is sufficient to remove moisture. Have attempts been made to determine the residual moisture in the used PET flakes? If the presence of moisture above the permissible values is found, How would they change the results obtained?

4. Conclusion

According to 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 Simona Zahova.

Date: 12.02.2025 **Reviewer:**

Member of the Academic Jury