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Review report on the doctoral thesis of M.Sc. Joanna Brzoska entitled "Synthesis and chemical structure of polyurethane materials obtained with the use of bio-based isocyanates"

The doctoral dissertation of M.Sc. Joanna Brzoska submitted to me for review, was carried out at Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology under the supervisor of Prof. Janusz Datta, D.Sc. and co-supervisor Ewa Głowińska, Ph.D.

Selection of research topics

The increasing consumption of non-renewable natural resources, including oil, as well as economic, political and ecological considerations, are prompting a new approach to the production of synthetic polymers among other polyurethanes. Polyurethane materials are characterized by a number of unique physicochemical properties that make them a subject of considerable interest in materials engineering. They exhibit extraordinary flexibility while maintaining high mechanical strength. The versatility of the properties of polyurethanes means that demand for them is growing and their consumption is constant. Polyurethanes have a wide range of applications in many areas, especially in the clothing and footwear

industry, upholstery, construction, automotive and paint industries as well as in the production of everyday products.

The production of polyurethanes is predominantly based on petrochemical feedstocks. Variations in the availability and pricing of crude oil may lead to challenges in securing these resources, potentially constraining the synthesis of monomers essential for polyurethane production. Moreover, the extensive reliance on fossil-derived raw materials poses significant environmental risks. Consequently, there is a growing imperative to incorporate biomass-derived alternatives, which can contribute to the reduction of greenhouse gas emissions and overall environmental pollution. In this context, it is essential to advance research focused on the development of bio-based polyurethanes, which can significantly alleviate the dependency on petrochemical-derived materials. A key issue in bio-based polyurethanes is the use of isocyanates obtained from renewable sources in reactions with limited reliance on toxic phosgene.

Taking the above issues into consideration, I am convinced that the research topic chosen by the Doctoral Student, concerning the impact of natural raw materials on the chemical structure, morphology, and selected properties of the resulting bio-polyurethanes, is both highly relevant and perfectly aligned with contemporary scientific challenges. The work makes a significant contribution to the development of bio-based polyurethane technology, particularly in the synthesis of isocyanates containing 100% renewable carbon. This research approach is not only relevant but also essential for the continued advancement of scientific knowledge and technological innovation. The presented research approach is not only timely but also essential for the further development of knowledge and technological innovation. I believe that the topic of the doctoral dissertation, concerning the synthesis and characterization of polyurethane materials using bio-based isocyanates, is fully justified and perfectly fits within the scope of more environmentally friendly polyurethane production.

Formal and substantive evaluation of the dissertation

The submitted doctoral dissertation of M.Sc. Joanna Brzoska, is based on four thematically coherent scientific articles published in specialist journals such as: Scientific Reports, Industrial Crops and Products, Green Chemistry and International Journal of Molecular Sciences published in renowned scientific publications with a combined IF of 24.9 and a

MNiSW score of 680. IF values and MNiSW scores have been provided based on the MOSTWIEDZY. It should be emphasized that the PhD student is the first author in the papers, and the contribution of the co-authors of the publications has been clearly defined in the declarations attached to the dissertation. Percentage contribution of the PhD student in the papers is in the range of 70-40%.

The dissertation consists of four sections (167 pages) including theoretical framework, aim and scope of the research, enclosed scientific publications and summary preceded by the list of publications serves as the foundation for doctoral dissertation and list of abbreviation and acronyms. The first section is an excellent introduction to the issues related to the chemical structure of polyurethanes, their synthesis methods and petrochemical monomers used in their production. It is worth noting that the characteristics of the commonly used isocyanates include their current market and forecasts. The Author presented clear recommendations regarding the use of isocyanates and the resulting need to introduce of renewable bio-based products which reduce footprint carbon. In the following chapter, the Doctoral Student conducted a literature review on bio-based and zero-emission monomers, highlighting that current trends focus on phosgene-free isocyanate synthesis methods using natural, renewable resources such as vegetable oils.

The next chapter presents the current state of the art in fully bio-based polyurethanes. The literature review clearly indicates that the production of polyurethanes based entirely on biomass products remains a significant challenge, especially in terms of obtaining materials with properties similar to polyurethanes obtained on conventional polyurethanes. A particularly important aspect is the departure from the methods of isocyanate synthesis based on the reaction of amines with toxic phosgene and its derivatives. The literature review was well thought out and written. The doctoral student comprehensively discussed the current state of knowledge regarding the issues that are the subject of her dissertation. The in-depth analysis of existing literature clearly supports the relevance of the chosen doctoral research topic, which is closely related to the development of innovative bio-based polyurethane materials.

The PhD student also pointed out that the use of naturally derived isocyanates presents a significant technological challenge due to specific safety and environmental

requirements. The literature review conducted by the doctoral student is based on 97 well-selected and up-to-date literature sources.

The next part presents the scope of the research conducted. The main objective of the study was to obtain polyurethane materials and to characterize them using reagents of natural origin, with the aim of reducing the consumption of non-renewable resources and limiting greenhouse gas emissions. The specific objectives of the doctoral thesis included the synthesis and modification of bio-based isocyanates to serve as key components in polyurethane production, as well as the evaluation of their impact on various properties of the resulting polyurethanes, with particular emphasis on their chemical, mechanical, and thermal characteristics. The research tasks included in the doctoral dissertation concerned the synthesis of urethane prepolymers, modification of triisocyanate, phosgene-free isocyanate synthesis, and the synthesis of bio-based polyurethanes. The results of the first, second, and fourth tasks were described in the publications attached to the dissertation. The research conducted by the PhD student as part of her dissertation also resulted in a patent application (No. P.446662) entitled "Cast polyurethane with increased content of bio-based carbon and its production method". The method of phosgene-free isocyanate synthesis was described in detail in the dissertation. The materials 1,4-diisocyanatobutane and 1,8-diisocyanatooctane obtained by the doctoral student via the Curtius rearrangement have not yet been published.

The third section of the doctoral dissertation contains the scientific articles on which the doctoral dissertation is based, along with the authors' statements. Of the four attached articles, the first one is a review paper and the other three are original papers concerning the PhD student's own research. The review paper concerns information on biologically derived materials used as an alternative to products from non-renewable energy sources for the production of isocyanates. In addition, the toxicity of isocyanates of petrochemical origin and using phosgene was discussed. The advantages and disadvantages of currently used methods for the production of isocyanates were also presented, which are relevant to the scalability of production. An important element that should be taken into account is the policy of sustainable development and reduction of toxicity.

The second paper concerns the synthesis and characterization of new bio-derived urethane prepolymers based on bio-based isocyanate Tolonate X FLO 100 monomer and two types of polyols, i.e. polyether (Velvetol H2400) and polyester (PRIPLAST 3294), also derived from renewable materials. The materials obtained by the PhD student were examined using the following methods: the FTIR and NMR methods were applied for the determination of their chemical formulas and structure, as well as thermogravimetry methods and rheological measurements due to characterization of their thermal stability and processability. It has been demonstrated that the origin of the polyols and the NCO content influence the prepolymer's properties.

The third paper presents the results concerning the synthesis and characterization of bio-based polyurethanes obtained with using bio-based: polyester polyol (PO3G) or polyether polyol (Priplast 3294) and partially bio-based isocyanate (Tolonate X FLO 100) with also bio-based 1,3-propanediol as chain extender. As reference materials, polyurethane based on the petrochemical monomers were produced. Confirmation of the chemical structure of the polyurethanes was achieved through FTIR-ATR and NMR spectroscopy. Thermogravimetry method allowed to doctoral student to determine thermal stability as well as influence of temperature on their behavior. Two step degradation of the materials is connected with the decomposition of at first of hard segments containg mainly isocyanates and chain extenders while the second step is due to the decomposition of polyol chains. The bio-based polyurethanes demonstrate a slightly lower stability in comparison to the petroleum derived reference material. The DMTA measurements point out that bio-based polymers are more flexible than reference one.

In the next attached article, the PhD student describes the results of her research on the solvent-free synthesis of bio-based polyurethanes using bio-based commercial isocyanate Desmodur eco N 7300 modified with Cardolite NX-2026 and bio-based and petrochemical polyols. The obtained materials were characterized by green carbon content in the range of 44-88%. The DSC and XRD methods confirmed the amorphous character of the obtained biobased polyurethanes. Their thermal stability and pathways of thermal degradation were determined based on the thermogravimetric analysis. Mechanical, thermomechanical, density and swelling properties of the polyurethanes show that they may be used as transparent and soft coating materials.

Section four presents a summary of the research findings. The dissertation is concluded with a compilation of the doctoral candidate's scientific accomplishments, research collaborations, and organizational involvement. The doctoral student's total scientific achievements include: 6 scientific articles from the JCR list, a scientific article from outside the JCR list, 1 patent granted, 2 patent applications, 2 oral presentations at national and international conferences, 6 posters in which the doctoral student was the presenter and 8 posters as a co-author. It is worth emphasizing that the doctoral student participated in a research project WEAVE-UNISONO entitled: “Sustainable polyurethanes "from the cradle to the grave" using enzymes” and part of the results of the doctoral dissertation were obtained as a result of its implementation. Ms. Brzoska also received awards for the best poster and presented inventions at international events. In addition, she was a laureate of scholarships at the Gdańsk University of Technology and within the IDUB program. The doctoral student also completed two research internships. The PhD student can also demonstrate extensive organizational activity, including organizing of the 15th Conference on Thermal Analysis and Calorimetry (2024) in Zakopane and the conference “Zastosowanei sprzężonych metod analizy termicznej w badaniach materiałów (2023) in Gdańsk and participating in events promoting science (The Baltic Science Festival in 20121-2024).

The scientific articles forming the foundation of the doctoral dissertation have already undergone a rigorous peer-review process and have been positively evaluated. I would kindly ask the PhD student to address the following questions during the defense of the dissertation.

1) The doctoral dissertation includes a detailed description of phosgene-free isocyanates synthesis that has not yet been published. I am curious whether the diisocyanates obtained through this method have been studied using any methods other than NMR, and if so, which ones. I would greatly appreciate a brief presentation of these methods.

2) Can the decomposition mechanism of the synthesized polyurethanes, which assumes that the stages are closely related to the decomposition of hard and soft segments, be easily confirmed based on the TG-FTIR spectra of the gaseous decomposition products of polyurethanes?

3) I am curious about your personal opinion on the possibility of completely replacing petroleum-based polyurethanes with bio-based polyurethanes. Whether bio-based polyurethanes will be able to fully replace them?

Final conclusions

In conclusion, I can confidently affirm that academic background of M.Sc. Joanna Brzoska is excellent. The PhD student has thoroughly reviewed the current state of knowledge regarding the production of polyurethanes, which allowed her to clearly define the research objectives and successfully achieve them. Based on the conducted analysis of the doctoral dissertation, I believe that this work meets high scientific standards. The author has demonstrated extensive knowledge, research skills, and scientific independence. The dissertation addresses important and current research topics concerning devolping of the synthesis methods of bio-based polyurethanes in a research area that has been relatively unexplored. The obtained results are highly innovative and aligned with the policy of sustainable development and carbon dioxide emission reduction.

The doctoral dissertation submitted for review entitled **„"Synthesis and chemical structure of polyurethane materials obtained with the use of bio-based isocyanates"** meets the statutory criteria for doctoral thesis set out in the Act of 20 July 2018 The Law on Higher Education and Science (Journal of Laws of 2018, item 1668 with later amendments). On this basis, I am applying to the Council of the Discipline of Chemical Sciences of the Gdańsk University of Technology to admit M.Sc. Joanna Brzoska to the further stages of the doctoral procedure.

At the same time, in accordance with the rules for recommending a doctoral dissertation for distinction in the discipline of Chemical Sciences at Gdańsk University of Technology, I hereby propose that the doctoral dissertation of M.Sc. Joanna Brzoska be awarded with distinction. The basis for this recommendation is the development of an innovative solution concerning the modification of isocyanates for the production of polyurethanes, which has been documented in a patent application.

R. Łyszczek