Warsaw University of Technology
Faculty of Chemistry

Warsaw, 08.06.2025

Andrzej Plichta, PhD, DSc, Associate Professor
Chair of Chemistry and Technology of Polymers

Review of the doctoral dissertation
'*Synthesis and chemical structure of polyurethane materials obtained with the use of bio-based isocyanates*'
in the proceedings for the award of the doctoral degree Ms. Joanna Brzoska, MSc, performed under the supervision of Mr. Janusz Datta, PhD, DSc, Associate Professor and Ms. Ewa Głowińska, PhD, serving as auxiliary supervisor.

Introduction. This review was prepared at the request of the Chairman of the Discipline Council of *the Chemical Sciences of the Gdańsk University of Technology,* Mr. Marek Tobiszewski, PhD, DSc, Associate Professor, included in letter No L. Dz. 102 CH/Dz/2025 of 8 April 2025. The opinion was prepared on the basis of the submitted doctoral dissertation in the form of a collection of 4 scientific publications in journals from the JCR list (along with statements of co-authors about their own contribution to each publication) preceded by a theoretical introduction and the purpose and scope of research.

The review was prepared on the basis of the provisions of the Act of 20 July 2018 - Law on Higher Education and Science (Journal of Laws No. Journal of Laws 2023, item 742 as amended). In addition, the guidelines contained in the guide "Reviews in proceedings for scientific promotion. Guide" published by the Council for Scientific Excellence in 2022.

The subject of the dissertation. The doctoral dissertation submitted for review concerns research on the synthesis and modification of isocyanate monomers from renewable sources (bio-based), and then their use in obtaining polyurethanes (PU) on their basis and the study of the impact of these monomers on the physico-chemical properties of polymers. Although the history of PU began as early as the fourth decade of the twentieth century, these polymers still occupy an important position in both the application and scientific areas. This state of affairs results from the possibility of broad control of their chemical, thermal and material properties by the selection of appropriate raw materials (monomers and additives), their relations and process parameters. Therefore, it is possible to obtain thermoplastic or cross-linked PUs, which may have different elasticity/stiffness, be solid or foamed and additionally physically modified. The main substrates in the additive synthesis of typical PUs are polyols (bi- or polyhydric), di- or polyisocyanates and chain extenders, and the synthesis process itself is based primarily on the reaction of isocyanate groups with hydroxyl ones. The chemical structure of these components and the molar mass of polyols and the molar ratios of polyols to chain extenders fundamentally affect the chemical resistance and physical properties of the PU, associated with its ability to form flexible (soft) and rigid (hard) phases. Important segments of PU applications are rigid and flexible foams as well as one-component adhesives containing moisture-curing urethane prepolymers. It is also worth mentioning the non-isocyanate PUs that have been under development for some time, which are most often based on the reaction of cyclic biscarbonates with diamins. Most of the PU systems available on the market are based on petrochemical raw materials, while due to the growing climate problem, including carbon dioxide emissions, systems based on renewable raw materials should be sought, while in the case of polyols and

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

chain extenders such alternatives are already available, in the case of diisocyanates the advancement of research is at a much lower stage. This is a significant scientific and then technological problem, and at the same time a considerable challenge for scientists to solve. This challenge was taken up by Joanna Brzoska in her work.

The aim of the doctoral thesis, defined by the doctoral student, was related to the development and study of methods of synthesis of PU with an increased share of raw materials of natural origin, with particular emphasis on innovative methods of modification and unconventional ways of obtaining isocyanates, which is in line with the current aspirations of the chemical industry to reduce fossil fuel consumption and carbon dioxide emissions.

Summing up the above, I conclude that the title of the dissertation is consistent with the presented purpose of the dissertation and is adequate to the content presented in the literature section and the publication cycle.

Characteristics of the dissertation. The dissertation was prepared in English in the form of a 167-page manuscript (including reproductions of scientific articles). In addition to formal elements (e.g. statements) and personal elements (e.g. thanks), the dissertation contains a table of contents, a list of publications that make up the doctorate, a list of abbreviations and following chapters:

I. Theoretical framework
II. Aims and scope of the research
III. Scientific publications
IV. Summary

Below the above numbered chapters are discussed:

I. *Theoretical framework.* The chapter presents the classification of PU, their applications and a detailed analysis of the impact of chemical structure on the performance of materials, with particular emphasis on the role of soft and hard segments. The importance of the molar ratio of isocyanate to hydroxyl groups, which determines the mechanical properties and thermal resistance of the final products, was discussed. The differences resulting from the use of different types of polyols (e.g. polyether and polyester) and their petrochemical or natural origin were discussed. Particular attention was paid to isocyanates, including petrochemical origin and commercially available offer of bioisocyanates, indicating their properties, carbon content from renewable sources. Numerous examples of research on bioisocyanate-based PUs are presented. Phosgen-free reactions used in the synthesis of bioisocyanates, including rearrangement of Curtius, Hofmann and Lossen, were also discussed in detail. Restrictions related to their implementation on an industrial scale were identified, including low efficiency, difficulties in product purification. The synthesis and properties of PU formed with the use of bioisocyanates (e.g. LDI, PDI, HDI). Depending on the synthesis method used (one-step or prepolymer-based), the studies demonstrated varying performance parameters, including glass transition temperature, flexibility, mechanical strength, chemical resistance, and thermal stability. Particular attention was paid to the relationship between chemical composition and application potential, especially in biomedicine (e.g., drug delivery systems, cell scaffolds), construction (rigid foams, protective coatings), and the footwear and automotive industries (elastomers, flexible foams). Comparisons with conventional polyurethanes (PU) indicate that bio-based alternatives can offer comparable or even superior physicochemical and functional properties.

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

The chapter concludes by emphasizing that, despite the growing availability of bio-based polyols and the initial successes in commercializing bio-based isocyanates, the development of sustainable polyurethanes still requires further intensive research and close collaboration between industry and academia. Key challenges include increasing synthesis efficiency and purity, scalability of technologies, raw material availability, and process safety. The chapter ends with a reference list comprising 97 sources.

II. *Aims and scope of the research*. The chapter defines the purpose of the work as the development and study of methods of synthesis of PU materials with an increased content of raw materials of natural origin. The PhD student notes that the goal is in line with the current activities of the chemical industry aimed at reducing the use of fossil fuels and carbon dioxide emissions. The dissertation pays special attention to isocyanates - the key compounds used in the synthesis of PU - whose modifications and alternative methods of obtaining are an important area of interest for science and industry. The scope of work included, therefore, synthesis (by a method without the use of phosgene) and modification (triisocyanates) of bioisocyanates as basic components in obtaining PU, as well as assessment of the impact of renewable raw materials used on chemical, mechanical and thermal properties of obtained PU.

III. *Scientific publications*. The chapter consists of a set of 4 reproductions of scientific publications constituting the basis of the dissertation. Before each publication, descriptive and percentage information about the author's contribution to the creation of a given publication was placed, including the stage of planning and conducting research. Following each publication, similar signed declarations from all co-authors were included. The reviewer found a convergence of statements both in terms of the description of the contribution and its estimation as a percentage for all 4 publications. The following briefly discusses the most important conclusions of the research and their importance for the development of the discipline, in relation to each publication.

1. *Challenges and recent advances in bio-based isocyanate production*. This publication is a review article. The description refers to the current state of research on the use of raw materials of biological origin for the synthesis of isocyanates. It was noted that in the literature there is a clear increase in interest in bioisocyanates as an alternative to traditional isocyanates of petrochemical origin, and raw materials such as vegetable oils, lignin or amino acids are a promising source of compounds with a high content of renewable carbon and a low carbon footprint. The article reviews the existing methods of obtaining isocyanates from biomass, taking into account their advantages and limitations. Particular attention was paid to the risks associated with the use of phosgene and the need to eliminate it in the pursuit of sustainable PU synthesis. The issues of technical and economic barriers related to the production of bio-monomers on an industrial scale were also raised. The importance of further technology development, implementation of sustainable development policies and consumer education was also stressed. The use of mixtures of conventional isocyanates and bio-derived isocyanates to optimise costs while increasing the share of renewable raw materials without degradation of material properties was identified as a possible transitional direction. The study is a valuable state-of-art for scientists from the discipline and related disciplines dealing with biomaterials, including bioisocyanates and bioPU. At the same time, it should be noted that a significant part of the information contained in this publication has already been presented by the doctoral student in the first chapter, which is also confirmed by about 25 common sources. It is

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

therefore worth considering whether the theoretical introduction in its present form was a necessary element of the dissertation.

2. *Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties*. The publication describes research on urethane prepolymers obtained entirely from commercial bio-raw materials: polyetherols and polyestrols and isocyanates. The exact structures of both isocyanate and polyestrol have not been unambiguously disclosed by the manufacturers, which significantly hinders the analysis of the products obtained. The doctoral student studied structural changes resulting from the chemical reaction between these components based on spectrometric methods: FTIR and NMR. In the case of infrared analysis, the response was assessed on the basis of changes in the relative intensity of the substrate bands and the occurrence of new product-specific bands. Due to the lack of structural information, the analysis by H NMR was limited to observations analogous to those made using FTIR spectroscopy, with the distinction that proton signals were examined. The spectra could not be interpreted in a typical, comprehensive manner. The extent of the reaction was assessed primarily based on the appearance of a signal around 8.5 ppm, attributed to protons adjacent to the nitrogen atom in the urethane group. According to the reviewer, this signal was also visible on the isocyanate spectrum. Changes in the signal integrals were not evaluated by the author. The omission of this type of analysis did not allow to fully exploit the potential of spectroscopic data, which in the case of research in the field of chemical sciences could help in the interpretation of results and bring significant cognitive value. The rheological analysis revealed differences in viscosity depending on the composition and molar ratios of the reactants. It was found that the resulting prepolymers behave as shear-thickening fluids and exhibit thixotropic properties. These studies also enabled the description of the results using appropriate rheological models. It would be interesting to study the rheological properties during a chemical reaction, which could further confirm its course and determine the moment of completion. In the next step, the thermal stability of prepolymers was tested by the TGA method under pyrolytic conditions. The authors suggest that hardened PU was also studied, however, the reviewer did not find information on how prepolymers were hardened (chain extended) or specific results of thermal stability of the PU. A multistage decomposition of prepolymers was found due to the presence of isocyanate groups, while polyols decomposed in one step at higher temperatures. Based on the conducted research, it was found that the type of bio-polyol used (polyether vs. polyester) significantly affects the viscosity and thermal stability of prepolymers - polyester prepolymers were characterized by significantly higher viscosity and better resistance to thermal degradation. Thanks to the ability to regulate properties through the selection of components and synthesis conditions, these prepolymers are a promising material for the industrial production of PUs with high flexibility, abrasion resistance and vibration damping capabilities, including the RIM method. Research on sustainable material solutions, based on the use of renewable raw materials, is an important contribution to the development of the discipline of chemical sciences, providing knowledge on the impact of the structure of bio-derived-raw materials on the properties of urethane prepolymers. An important shortcoming of the research in this publication is the lack of PU material tests obtained after the curing of these prepolymers.

3. *A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates*. The paper investigates the properties of four PUs obtained from two bio-

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

polyols and two petrochemical origins in reaction with bio-isocyanate chemically modified with CARDANOL. The modification was aimed at reducing the functionality of isocyanate, leading to less cross-linked polymers and increasing the share of bio-components in the PU. The polymers were obtained by the prepolymer method, using bio-1,3-propandiol as a linker for hard segments (chain extender). Based on the FTIR spectra, the structure of the synthesized PUs was confirmed, among others, through the -NCO group bands. The deconvolution analysis of the carbonyl band made it possible to assess phase separation and mixing, showing that phase separation was predominant (above 50-70%). Thermal analyses were carried out showing differences in thermal stability depending on the diol used and analyzing Tg, visible for most samples only from rigid segments (46-56 °C) and in 1 case for the elastic segment. The materials did not show melting of crystalline structures (DSC, confirmed by XRD). Tg of elastic segments was determined by DMA analysis method (-57 to -2 °C). On the same basis, it was found that all materials had good damping properties (high tanδ values). The analysis of the storage modulus shows that the structure of soft segments affects the thermomechanical properties of bio-PU materials. The highest stiffness was exhibited by materials based on petrochemical ester polyol and the bio-based PPG polyol. Analysis of the mechanical property data indicated that the type of polyol and the chemical structure of the soft segments influence phase separation, which plays a key role in shaping the mechanical properties of polyurethanes. Bio-based PUs offer greater flexibility, whereas petrochemical segments contribute to higher hardness and improved mechanical strength. The obtained materials were characterized by relatively low static tensile strength (up to 1.5 MPa) and low for PU elastomers deformation (<100%) especially in relation to typical PU. The tested PUs did not degrade in acetone (a polar solvent) or in toluene (a non-polar solvent), confirming their crosslinked structure. Swelling was observed, with its extent depending on the type of polyol and the polarity of the solvent. Acetone interacted more strongly with the more polar segments, leading to greater swelling, whereas toluene penetrated the material to a lesser extent. The density of all samples fell within the typical range of 0.9–1.1 g/cm^3, indicating proper crosslinking and consistency with literature data. In conclusion, the use of a modified bio-based isocyanate enabled the production of bio-PUs with high transparency and softness.

4. *The influence of bio-based monomers on the structure and thermal properties of polyurethanes*. As in the previously described publication, the authors examined the effect of bio-ingredients on the properties of the obtained PU. A total of 6 compositions were examined, of which 2 were based 100% on ingredients of petrochemical origin, another 2 used petrochemically obtained diols and bio-isocyanate along with bio-diol chain-extending the urethane prepolymers obtained in the first stage, as well as 2 systems using only raw materials with bio-content. The resulting PUs were characterized in almost the same way as in Publication No. 3, with the addition of the Small Angle X-ray Scattering (SAXS) method, which revealed that the PU samples showed two peaks, corresponding to the separation of the soft segments and the structure of the hard segments. In petrochemical isocyanate (HDI) samples, peaks move toward higher Q values, indicating a more compact structure and smaller domains. The weaker intensity of the second peak suggests a lower content or ordering of the hard segments. PU analysis using H NMR spectrometry is presented in this publication in a more methodical way than in the others, along with the precise assignment of signals in the spectrum to the protons of the polymer structure. Moreover, it was found that samples obtained with petrochemical diisocyanate show in

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

DSC, in addition to the melting of the crystalline elastic phase (soft), additional melting of the rigid phase (hard), which is consistent with the WAXS results, indicating the presence of more complex and orderly crystal structures in these samples (additional diffraction peak). The TGA analysis showed that all PU samples underwent two-stage thermal degradation – the first stage was related to the distribution of hard segments and the second was related to the distribution of soft segments. Bio-PUs showed slightly lower thermal stability than petrochemical-based samples, and polymers containing polyether polyols were more thermally stable than those with polyester soft segments. In addition, it was found that bio-isocyanate, gives PU with lower stability than HDI, which is associated with the branched structure of the bio-based one. A valuable extension was the use of the TGA method coupled with FTIR, on the basis of which it was assessed that during the thermal decomposition of PU, regardless of their origin, carbon dioxide and compounds containing aliphatic groups (methylene and methyl), as well as primary hydroxyl groups (alcohols) are formed. The conducted research demonstrated that it is possible to obtain PUs with a high bio-based carbon content (up to 52%) without negatively affecting the synthesis process. Moreover, these materials can be cured at lower temperatures, making the process more economical and energy-efficient. Although the bio-based PUs exhibit lower crystallinity (as confirmed by SAXS and WAXS) and slightly reduced thermal stability (TGA), DMTA tests showed that they are more flexible than samples derived from petrochemical feedstocks, which may be advantageous in applications requiring high deformability.

IV. *Summary*. As part of the doctoral dissertation, bio-PU synthesis was developed and carried out with a green carbon content of 44% to 100% (declared value, not confirmed by publication or detailed results), which is an important contribution to the development of sustainable synthesis and material technologies. The PhD student focused on bioisocyanates-as a key but still underdeveloped element in the field of green PUs. The author managed to apply three approaches to the use of bio-isocyanates:

(a) the use of commercial bio-isocyanate,

(b) its modification in order to control the functionality and increase the green carbon content,

(c) synthesis of BDI and ODI bio-isocyanates by the Curtius method using a safer agent, diphenylphosphoryl azide, as an alternative to sodium nitride.

The overall results of the research described in point (c) together with the results of the synthesis of PU based on these isocyanates were not presented in the content of the dissertation or in the form of a published or sent for review manuscript. Therefore, despite the author's declaration, it is difficult to consider this stage of work as fully completed or documented. A number of modern analytical methods were used to characterize the obtained materials. All polyaddition reactions produced fully reacted PUs, which showed good thermal stability in the range of 237-299 °C, sufficient for most typical PU applications. PU-specific degradation processes were also observed in 2-3 steps, and the physicochemical properties of the materials depended on the raw materials used. Bio-PUs were characterized by greater flexibility, slightly lower thermal stability, lower crystallinity and lower mechanical strength compared to petrochemical counterparts. Some of them were completely or partially transparent.

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

General remarks. The submitted doctoral thesis takes up a current and important topic related to research on the synthesis and properties of PUs derived in part from renewable raw materials (both, related to polyol and isocyanate), which makes it a valuable contribution to the development of knowledge in the discipline of chemical science. The research methods used, including analytical and microscopic techniques, were appropriately selected to solve the problem posed, and the experiments were conducted properly, which allowed to obtain consistent results. The entire dissertation, including its publications, testifies to the author's ability to conduct scientific research independently and effectively plan and implement complex experiments, which emphasizes the high substantive level of the dissertation.

The titles of the chapters and sub-chapters are adequate to the content presented in them. The dissertation, including publications, is illustrated, which greatly facilitates reading and usually draws appropriate conclusions. Drawings, including chemical formulas and equations presented in the dissertation and the publications, are prepared in a clear and aesthetic way. The nomenclature used is correct and typical of the English language. I appreciate the editorial side positively.

In the reviewer's opinion, the dissertation lacks a clear guide to the scientific publications on which the research is based. While the final summary of the dissertation could potentially serve this purpose, its scope is too limited to fulfill this role adequately.

Evaluation of the Achievements Presented in the Dissertation. In conclusion, I believe that the submitted doctoral dissertation presents important research results, correct discussion of results and correct conclusions on topics of great scientific importance in the discipline of chemical sciences. In addition:

1. based on the analysis of the content of the chapter *SECTION I THEORETICAL FRAMEWORK* of the doctoral dissertation, literature introductions in the attached publications and, above all, the review publication *Challenges and recent advances in bio-based isocyanate production* (all elements discussed in this review), I conclude that the doctoral dissertation presents the general theoretical knowledge of Ms. Joanna Brzoska in the discipline of chemical sciences, especially in the field of PUs, in particular synthesized with the participation of bio-raw materials, methods of obtaining these raw materials as well as bio-PU, and their properties. The PhD student prepared literature reviews with high scientific maturity, she included all aspects important from the point of view of her own research, basing them on a large number of literature references. She is fluent in scientific literature in English and critically analyzes literature reports.

2. based on the analysis of the content of the publication *Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties*, *A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates* and *The influence of bio-based monomers on the structure and thermal properties of polyurethanes* which form part of the doctoral dissertation (and are discussed in this review, including the general remarks herein), I conclude that the dissertation demonstrates Ms. Joanna Brzoska possesses the ability to conduct independent scientific research. The doctoral candidate appropriately defined the research problem and formulated the objectives of the work based on a thorough literature review. She subsequently planned, conducted, and analyzed a series of experiments using advanced instrumental techniques (including FTIR, NMR, DSC, TGA, DMTA, SAXS, WAXS, XRD, and rheological measurements), leading to the successful resolution of the stated research problem.

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl

3. based on the analysis of the content of the submitted dissertation (including 4 related publications), summarized in this review and taking into account the general comments from this review, I conclude that the doctoral dissertation of Ms. Joanna Brzoska is an original solution to a scientific problem. Systems examined in the work have not been the subject of research published in scientific or technical literature. As a result of the research, new bio-PUs with a high content of "green" carbon were developed and characterized, obtained using both commercial and modified bio-isocyanates. Although the applied research and synthesis methods were standard, the novelty of the dissertation lies in the unique selection and combination of raw materials, which have not been previously reported. The resulting materials exhibited complete reaction conversion, good thermal stability, varied phase behavior, high flexibility, and partial transparency. The developed bio-based polyurethanes may serve as a viable alternative to petrochemical materials in applications where flexibility and thermal stability are crucial, while also reducing the carbon footprint. The research aligns with the current trends in green chemistry and sustainable development, addressing the growing demand from industry for environmentally friendly materials. The objective of the dissertation has been fully achieved.

Final conclusion. Based on the evaluation of the achievements presented in the dissertation, as outlined in the previous section of this review, I conclude that the doctoral thesis submitted by Ms. Joanna Brzoska, MSc, meets all the requirements specified in Article 187 of the Act of 20 July 2018 – Law on Higher Education and Science. I therefore recommend that the dissertation be accepted for public defense and for further stages of the procedure leading to the awarding of the doctoral degree in the discipline of chemical sciences.

(Signature of the reviewer)

Ul. Noakowskiego 3,
00-664 Warsaw, PL
tel.: +4822 2345632,
e-mail:
andrzej.plichta@
pw.edu.pl