GDAŃSK UNIVERSITY
OF TECHNOLOGY

DOCTORAL DISSERTATION

Author of the dissertation: Joanna Brzoska, M.Sc.
Title: Synthesis and chemical structure of polyurethane materials obtained with the use of bio-based isocyanates
Supervisor: Prof. Janusz Datta, D.Sc.
Auxiliary supervisor: Ewa Głowińska, Ph.D.

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Imię i nazwisko autora rozprawy: mgr inż. Joanna Brzoska
Dyscyplina naukowa: Nauki Chemiczne

ROZPRAWA DOKTORSKA

Tytuł rozprawy w języku polskim: Synteza i struktura chemiczna materiałów poliuretanowych otrzymywanych z wykorzystaniem izocyjanianów pochodzenia naturalnego

Tytuł rozprawy w języku angielskim: Synthesis and chemical structure of polyurethane materials obtained with the use of bio-based isocyanates

Promotor *podpis*	Drugi promotor *podpis*
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Gdańsk, rok 2025

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The author of the doctoral dissertation: Joanna Brzoska, M.Sc.
Scientific discipline: Chemical sciences

DOCTORAL DISSERTATION

Title of doctoral dissertation: Synthesis and chemical structure of polyurethane materials obtained with the use of bio-based isocyanates

Title of doctoral dissertation (in Polish): Synteza i struktura chemiczna materiałów poliuretanowych otrzymywanych z wykorzystaniem izocyjanianów pochodzenia naturalnego

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Gdańsk, year 2025

Załącznik nr 2/1
do Zarządzenia Rektora PG nr 30/2022 z 14 kwietnia 2022 r.

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Autor rozprawy doktorskiej: Joanna, Brzoska

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Autor rozprawy doktorskiej: mgr inż. Joanna Brzoska

Tytuł rozprawy doktorskiej w języku polskim: Synteza i struktura chemiczna materiałów poliuretanowych otrzymywanych z wykorzystaniem izocyjanianów pochodzenia naturalnego

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Język rozprawy doktorskiej: angielski

Promotor rozprawy doktorskiej: prof. dr hab. inż. Janusz Datta

Promotor pomocniczy rozprawy doktorskiej: dr inż. Ewa Głowńska

Data obrony:

Słowa kluczowe rozprawy doktorskiej w języku polskim: poliuretany, izocyjaniany pochodzenia naturalnego, poliaddycja, przegrupowanie Curtiusa, surowce odnawialne

Słowa kluczowe rozprawy doktorskiej w języku angielskim: polyurethanes, bio-based isocyanates, polyaddition, Curtius rearrangement, renewable resources

Streszczenie rozprawy w języku polskim: Przemysł dąży w kierunku zrównoważonego rozwoju oraz ograniczenia wpływu materiałów na środowisko. Obecnie materiały poliuretanowe, które stanowią ważny segment rynku tworzyw sztucznych są otrzymywane w reakcji poliaddycji di- lub polizocyjanianów z poliolami oraz przedłużaczami łańcucha. Wymienione surowce wykorzystywane na skalę przemysłową są pochodzenia petrochemicznego. W związku z tym poszukiwane są nowe, przyjazne dla środowiska metody ich syntezy lub modyfikacji. Celem niniejszej rozprawy doktorskiej była synteza poliuretanów z izocyjanianów pochodzenia naturalnego. Cel zrealizowano przez wykorzystanie komercyjnie dostępnych surowców pochodzenia naturalnego, modyfikację trójfunkcyjnego izocyjanianu oraz syntezę izocyjanianu na drodze bezfosgenowej. W ramach pracy określono wpływ substratów pochodzenia naturalnego na strukturę chemiczną, morfologię i wybrane właściwości otrzymanych poliuretanów. Rozprawa doktorska oparta jest na czterech artykułach opublikowanych w czasopismach naukowych z listy JCR.

Streszczenie rozprawy w języku angielskim: The industry is moving towards sustainability and reducing the environmental impact of materials. Currently, polyurethane materials, which constitute a significant segment of the plastics market, are synthesized by the polyaddition reaction of di- or polyisocyanates with polyols and chain extenders. These industrial-scale raw materials are predominantly of petrochemical origin. Consequently, new environmentally friendly synthesis methods or their modifications are being explored. The primary objective of this thesis was to synthesize polyurethanes from bio-based isocyanates. This was achieved by using commercially available bio-based isocyanates, modifying a trifunctional bio-isocyanate and carrying out isocyanate synthesis via a phosgene-free route. The study investigated the impact of the natural origin substrates on the chemical structure, morphology and selected properties of the obtained polyurethanes. This thesis is based on four papers published in JCR-listed journals.

DESCRIPTION OF DOCTORAL DISSERTATION

The Author of the doctoral dissertation: Joanna Brzoska, M.Sc.

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Title of doctoral dissertation in Polish: Synteza i struktura chemiczna materiałów poliuretanowych otrzymywanych z wykorzystaniem izocyjanianów pochodzenia biologicznego

Language of doctoral dissertation: English

Supervisor: Prof. Janusz Datta, D.Sc.

Auxiliary supervisior: Ewa Głowińska, Ph.D.

Date of doctoral defense:

Keywords of doctoral dissertation in Polish: poliuretany, izocyjaniany pochodzenia naturalnego, poliaddycja, przegrupowanie Curtiusa, surowce odnawialne

Keywords of doctoral dissertation in English: polyurethanes, bio-based isocyanates, polyaddition, Curtius rearrangement, renewable resources

Summary of doctoral dissertation in Polish: Przemysł dąży w kierunku zrównoważonego rozwoju oraz ograniczenia wpływu materiałów na środowisko. Obecnie materiały poliuretanowe, które stanowią ważny segment rynku tworzyw sztucznych są otrzymywane w reakcji poliaddycji di- lub polizocyjanianów z poliolami oraz przedłużaczami łańcucha. Wymienione surowce wykorzystywane na skalę przemysłową są pochodzenia petrochemicznego. W związku z tym poszukiwane są nowe, przyjazne dla środowiska metody ich syntezy lub modyfikacji. Celem niniejszej rozprawy doktorskiej była synteza poliuretanów z izocyjanianów pochodzenia naturalnego. Cel zrealizowano przez wykorzystanie komercyjnie dostępnych surowców pochodzenia naturalnego, modyfikację trójfunkcyjnego izocyjanianu oraz syntezę izocyjanianu na drodze bezfosgenowej. W ramach pracy określono wpływ substratów pochodzenia naturalnego na strukturę chemiczną, morfologię i wybrane właściwości otrzymanych poliuretanów. Rozprawa doktorska oparta jest na czterech artykułach opublikowanych w czasopismach naukowych z listy JCR.

Summary of doctoral dissertation in English: The industry is moving towards sustainability and reducing the environmental impact of materials. Currently, polyurethane materials, which constitute a significant segment of the plastics market, are synthesized by the polyaddition reaction of di- or polyisocyanates with polyols and chain extenders. These industrial-scale raw materials are predominantly of petrochemical origin. Consequently, new environmentally friendly synthesis methods or their modifications are being explored. The primary objective of this thesis was to synthesize polyurethanes from bio-based isocyanates. This was achieved by using commercially available bio-based isocyanates, modifying a trifunctional bio-isocyanate and carrying out isocyanate synthesis via a phosgene-free route. The study investigated the impact of the natural origin substrates on the chemical structure, morphology and selected properties of the obtained polyurethanes. This thesis is based on four papers published in JCR-listed journals.

The completion of this thesis would not have been possible without the assistance and encouragement of numerous individuals. I would like to express my gratitude to them here.

A special expression of gratitude goes to my supervisor, **Professor Janusz Datta**, for giving me the opportunity to pursue my PhD, for his trust in my abilities, and for his continuous support and invaluable scientific guidance throughout this process.

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I am deeply grateful to **my parents, my sisters and my husband** for their unwavering support and for always being there when I needed them most. Their encouragement and belief in me, even in moments of doubt, have meant more than I can express.

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I dedicate this doctoral dissertation to my beloved Parents,
who have always believed in me,
supported me at every stage of my journey,
and continuously gave me strength to pursue my dreams.
Without your love and patience, I would not be where I am today.

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THE LIST OF PUBLICATIONS SERVES AS THE FOUNDATION FOR THIS DOCTORAL DISSERTATION

The basis of this dissertation is a series of four thematically related articles published between 2021 and 2024 in journals listed in the Journal Citation Reports (JCR) database, with a cumulative Impact Factor (IF) of 24,9 and a total of 680 MNiSW points. In all of these papers, I am the first author.

1. **Brzoska,** J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.
2. **Brzoska, J.**, Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.
3. **Niesiobędzka, J.**, & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.
4. **Niesiobędzka, J.**, Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.

IF values and MNiSW scores have been provided based on the MOSTWIEDZY (www.mostwiedzy.pl).

LIST OF ABBREVIATIONS AND ACRONYMS

bio-PU/PUR	bio-based polyurethane
DMA/DMTA	dynamic mechanical thermal analysis
DPS	degree of the phase separation
DPM	degree of the phase mixing
DSC	differential scanning calorimetry
DTG	derivative thermogravimetric
E’	storage modulus
E”	loss modulus
FTIR	Fourier-transform infrared spectroscopy
^{1}H NMR	proton nuclear magnetic resonance
HS	hard segment
%NCO	content of free isocyanate groups (%)
PDO	1,3 – propanodiol
PTMG	poly(tetramethylene ether) glycol
PO3G	poly(trimethylene ether) glycol
Priplast	semi-crystalline polyester polyol
PU/PUR	polyurethane
SS	soft segment
tan δ	loss factor
TGA	thermogravimetric analysis
XRD	X-Ray Diffraction

SECTION I

THEORETICAL FRAMEWORK

1. Introduction

Among polymers, polyurethanes (PUs) stand out for their versatile properties and wide range of applications. They are used in the engineering, electronics, automotive, upholstery, construction and clothing industries [1–5]. Figure 1 illustrates various applications of polyurethane. Their versatility has led to an increase in the size of the polyurethanes market, with its value growing from US$89.92 billion in 2023 to US$103.08 billion in 2024 [6]. Despite their widespread use, PUs raise concerns regarding their environmental and health impacts, and recyclability. PUs are mainly petroleum-based materials so their disposal usually ends up in waste incinerators or landfills [7]. This contributes to greenhouse gas emissions and environmental pollution [8]. Moreover, most of the monomers used in PU synthesis (e.g. isocyanates) are toxic, sometimes even carcinogenic or mutagenic [9–12]. The upward trend in the polyurethanes market is driven by the sustainability trend, which is reflected in the pursuit of energy efficiency in the construction industry, the automotive industry, and developments in the medical sector [13–18].

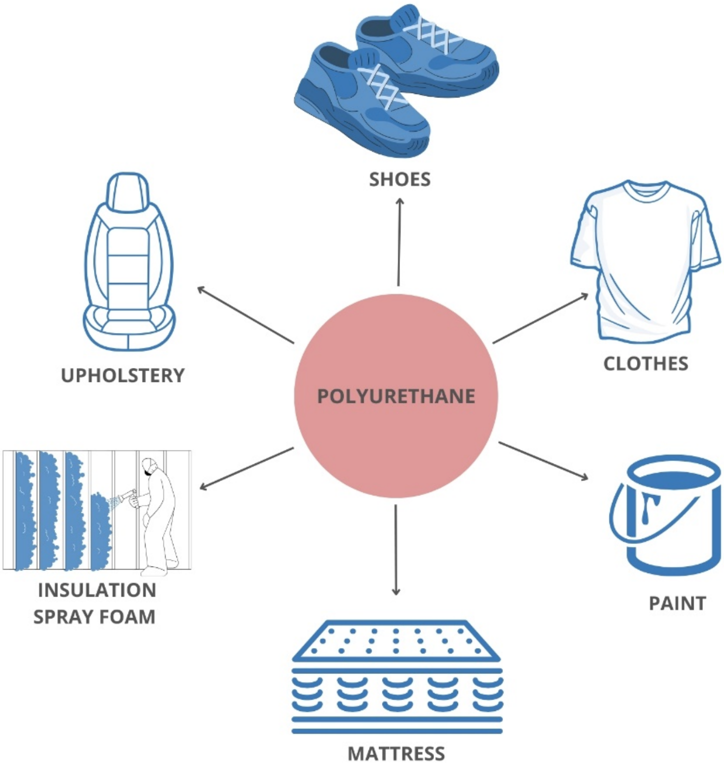


Figure 1. The following examples illustrate the diverse applications of polyurethane.

The production of polyols from natural raw materials has been widely described in the literature [19–22]. However, there is a lack of knowledge about isocyanates obtained from natural sources. Therefore, this thesis focuses on the synthesis of polyurethanes using isocyanates of natural origin. It has also investigated the modification of the trifunctional isocyanate to obtain cast polyurethanes. Furthermore, the synthesis of a phosgene-free isocyanate and the subsequent use of this isocyanate for the production of bio-based polyurethanes was explored. The study will investigate the influence of the bio-based substrates on the chemical structure, morphology and selected properties of the newly obtained bio-based polyurethanes.

1.1. Methods of polyurethane synthesis

The history of polyurethanes began in 1849 when Wurtz first obtained an isocyanate - the primary component in the synthesis of polyurethanes. Then in 1947, Otto Bayer obtained the first polyurethane material [23]. Since then, polyurethanes have been obtained by the polyaddition reaction of aromatic or aliphatic isocyanates with hydroxyl-containing compounds (e.g. diols) [24]. Figure 2 shows the reaction scheme for the synthesis of polyurethanes.

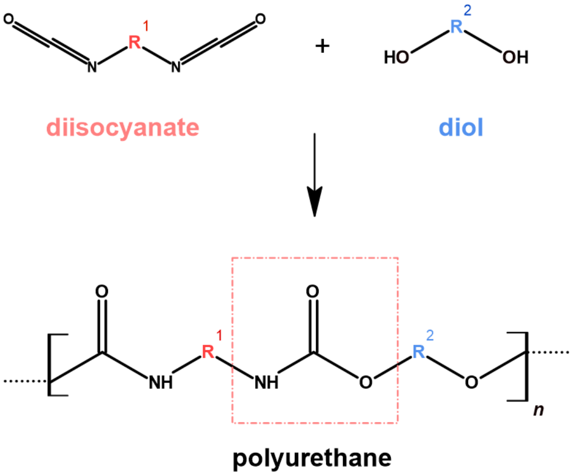


Figure 2. Schematic of the polyaddition reaction forming polyurethane from isocyanate and diol.

Polyaddition processes can be carried out in solvents or directly in bulk. Depending on the chosen method, the desired performance properties of the final product can be achieved. The two most commonly used methods for the synthesis of polyurethanes are: one-step and two-step (which is also known as prepolymer method). Both are based on the reaction of diisocyanates and polyols in the presence of a low molecular weight chain extender. However, the one-step process involves mixing all the reactants simultaneously. Whereas in the two-step method, a prepolymer is first obtained by reacting a polyol with an excess of di- or polyisocyanate. This results in an NCO-terminated chain which, in the next step, reacts with the functional groups of the chain extender. The prepolymer method tends to be more precise, with less mass dispersion and a higher degree of phase separation than the one-step method [25].

The high availability of raw materials for the production of polyurethanes makes it possible to obtain products with a wide range of physical and chemical properties. Multifunctional monomers can be used to obtain branched and cross-linked structures, while bifunctional monomers can be used to obtain linear polymeric structures. Linear polyurethane structures provide good mechanical properties such as flexibility and toughness, while cross-linked structures improve chemical and thermal resistance but reduce processability and flexibility. Meanwhile, polymers with higher degree of cross-linking can exhibit better thermal stability and mechanical performance. The properties of polyurethanes are closely linked to their segmented structure. They consist of alternating hard and soft segments [26]. A schematic of the PU chain structure is shown in Figure 3.

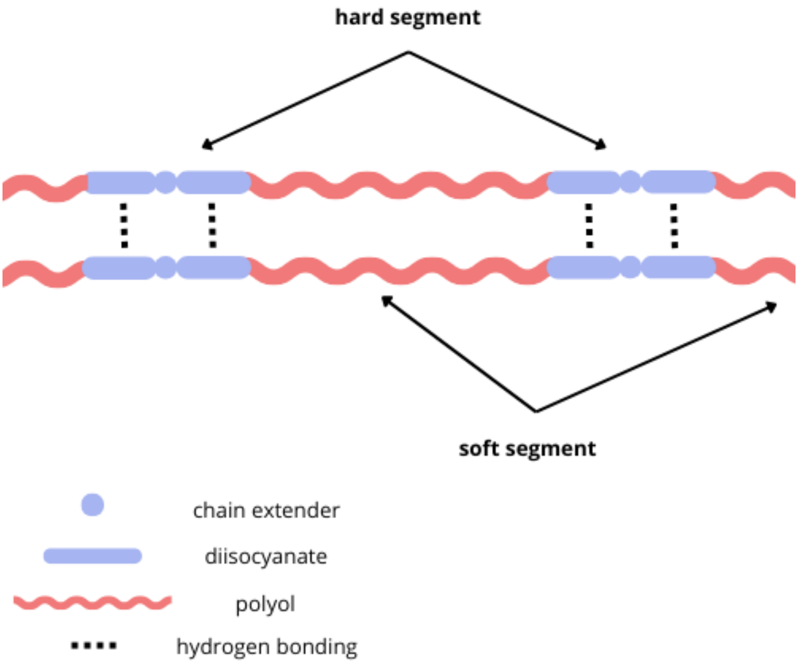


Figure 3. Scheme of a segmented polyurethane.

The soft segments are usually composed of polyols (e.g. polyether or polyester), which allow a certain degree of mobility due to their structure [27]. The hard segments, on the other hand, consist of an isocyanate and a chain extender [28]. The hard segments provide greater hardness, stiffness and abrasion resistance [29, 30]. Based on this, the properties of polyurethanes can be tailored: using longer-chain diols results in softer PU, while harder PU can be obtained by using low-molecular-weight polyols with high functionality or by significantly increasing the proportion of hard segments [31].

1.2. Petrochemical monomers

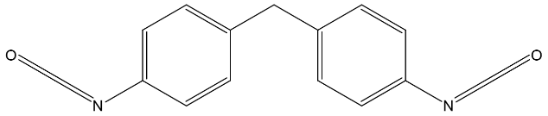
Although polyurethanes have many benefits, a key problem associated with their use is the substantial consumption of petrochemical raw materials and the use of hazardous isocyanates [32, 33]. Fluctuations in the availability and price of crude oil may lead to challenges in its procurement, potentially limiting the production of monomers used in polyurethane synthesis. Moreover, the extensive use of fossil raw materials poses a significant threat to the natural environment.

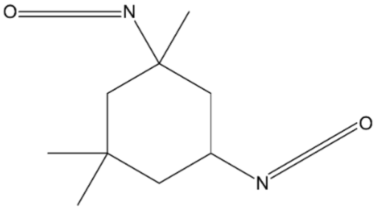
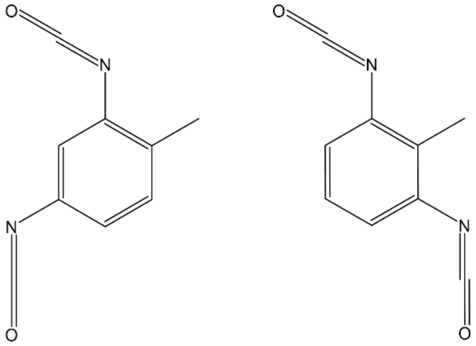
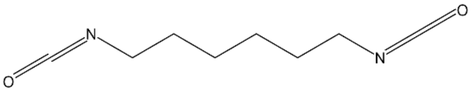
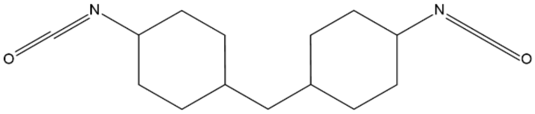
The most commonly used polyols in the synthesis of polyurethanes are polyethers and polyesters. Polyester polyols tend to be more expensive and more harmful [34]. However, the use of polyester polyols results in PUs with better abrasion, cut, and solvent resistance [35]. Meanwhile, polyether polyols remain flexible at low temperatures and have high resistance to UV radiation and water [36]. Examples of petrochemical polyols include: poly(tetramethylene ether) glycol (PTMG) polypropylene glycol (PPG), poly(ethylene oxide) (PEG) [37, 38], α,ω-oligo(ethylene-butylene adipate)diol (Polios 55/20) and poly(ethylene adipate) [39].

The second major component in the production of polyurethane is the isocyanate. Isocyanates can be divided into two main groups: aromatic and aliphatic. Aromatic isocyanates are inexpensive and provide good mechanical strength and reactivity. Unfortunately, they are prone to oxidation, which can lead to yellowing and poorer weather resistance. Aliphatic isocyanates, on the other hand, lack an aromatic ring, giving them better weather resistance and UV stability. The main aromatic diisocyanates are toluene diisocyanate (TDI), which consists of the isomers 2,4-TDI and 2,6-TDI, and 4,4’-methylenebis(phenyl isocyanate) (MDI). On the other hand, the most important aliphatic isocyanates are 1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI). HDI is mainly used in adhesives and coatings because of its resistance to yellowing when exposed to sunlight but is less reactive than TDI and MDI. TDI and polymeric MDI (pMDI) are the standard polyisocyanates used in polyurethane foam (PUF) formulations. pMDI is preferred for PUR due to its more homogeneous reaction kinetics and lowest vapor pressure, making it the safest to use. TDI, on the other hand, is used in open-cell polyurethane foams but is not suitable for cast PUR due to its inhomogeneous polymerization rate [40].

The most commonly used isocyanates are listed in Table 1. Their market size indicates the scale of their use and therefore the potential risk they can pose to worker health and the environment if not properly controlled.

Table 1. Examples of the most commonly used isocyanates, their structures and markets.

Name	**Structure**	**Market Volume**
4,4’-methylenebis (phenyl isocyanate) MDI		US$ 56 billion in 2024 to US$ 80 billion by 2033 [41]

Name	**Structure**	**Market Volume**
Isoprene diisocyanate IPDI		US$ 8.89 billion in 2024 to US$ 23.46 billion by 2031 [42]
Toluene diisocyanate 2,4-TDI 2,6-TDI		US$ 5.1 billion in 2024 to US$ 8.47 billion by 2033 [43]
1,6-hexamethylene diisocyanate HDI		US$ 10460 million in 2024 to US$ 11370 million by 2030 [44]
4,4′-Methylene-bis(cyclohexyl isocyanate) HMDI		US$ 31.87 billion in 2023 to US$53.48 billion by 2032 [45]

Furthermore, the industrial production of isocyanates is based on the use of phosgene, a highly toxic chemical that can be fatal in excessive doses [46–48].

As a result, the use of isocyanates has been restricted by the REACH Regulation. The purpose of the Directive was to supplement and amend the Registration, Authorisation and Restriction of Chemicals (REACH) Regulation for diisocyanates.

Regulation 2020/1149 on diisocyanates was introduced in two stages:

- from 24 February 2022, diisocyanates could only be placed on the market in concentrations of less than 0.1% by weight or if information on mandatory training for their safe use was provided. From 24 August 2023, a training statement will be required on the packaging.
- after 24 August 2023, diisocyanates can only be used industrially at concentrations below 0.1% by weight or after users have received mandatory safety training. Training must be documented and repeated every 5 years and suppliers must provide materials in the official language of the country of supply [49].

Against this background, the development of bio-based products for sustainable polyurethanes has been the focus of both research and industry. Bio-based products include vegetable oils such as corn, soybean, castor, rapeseed, and sunflower oils, as well as polysaccharides, polyhydric alcohols, fatty acids, and their derivatives [50]. In line with sustainable development, the use of renewable bio-based carbon feedstocks offers a reduced carbon footprint and improved Life Cycle Assessment (LCA). This means that more and more of the materials of the future will come from biomass [51].

1.3. Monomers and examples of bio-based polyurethanes

1.3.1. Bio-based and zero-emission monomers

The diversity of polyurethanes comes from the selection of raw materials, synthesis methods and monomer sources, leading to significant differences in their structural and functional properties. Currently, a wide range of monomers with diverse properties is available on the market. Bio-based equivalents of petrochemical substrates are also gradually becoming accessible. For instance, significant progress has been made in the production of polyols from natural raw materials. They can be obtained from various vegetable oils, including soybean, castor, and palm oils [52–54]. One study described the synthesis of a bio-polyol from soybean oil using ionic liquids through a ring-opening reaction of epoxidized soybean oil with glycerol as the nucleophile [55]. In an alternative study, polyol was synthesized from coconut oil using a solvent-free polycondensation method [56]. This polyol was subsequently combined with petrochemical isocyanate pMDI to produce naturally superoleophilic foam with inherent hydrophobic properties [57]. Scientists at Anhui Agricultural University have developed a way to use luffa seeds, which are considered agricultural waste due to their bitter taste. Luffa seed oil was used as the raw material and an epoxidation process was employed to obtain two types of polyols using diethylene glycol and methanol as ring-opening agents. These polyols and the petrochemical isocyanate (MDI) were then used to produce viscoelastic polyurethane foams [58]. The production of a cardanol-based bio-polyol is also known. The process involves a dual epoxidation of the phenolic -OH group and terminal unsaturation, forming cardanol monoglycidyl ether. This is followed by a ring-opening reaction, and the obtained bio-polyol is used in polyurethane formulations [59]. These are just a few examples of how to obtain naturally-derived polyols. In the Scopus database, a search for the phrase "bio-polyol" OR "bio-based polyol" returns almost 600 documents. There are also many commercially available bio-based polyols that are already widely used in industry. Commercially available natural polyols include: BiOH Polyols (Cargill), UPT 240 Premium (Polylabs), EMEROX 14050 (Emery Oleochemicals), Velvetol (WeylChem International), Priplast 3294 (Cargill), Lupranol Balance (BASF) and many others [60–65].

Simultaneously, isocyanates are produced mainly by the reaction of amine with phosgene, as shown in Figure 4. As mentioned earlier, phosgene is a toxic gas that was used as a chemical weapon during World War I. Its additional drawback lies in the fact that it is colorless and has a relatively mild odor, making its toxicity particularly insidious [66]. Furthermore, isocyanate degradation releases harmful substances such as diamines and hydrogen cyanide. These challenges have stimulated the search for sustainable, phosgene-free, bio-based alternatives, focusing on the development of isocyanates from renewable resources such as vegetable oils. Although alternative phosgene-free methods of producing isocyanates are known, Saunders and Slocombe described various approaches to isocyanate synthesis as early as 1948 [67]. The most widely used methods include the Curtius, Hofmann, and Lossen rearrangements. The Curtius rearrangement was developed to some extent by Schroeter who prepared various isocyanates by treating acid chloride with sodium azide and heating the product in a benzene solution [68, 69]. Curtius subsequently used this reaction to obtain ethylene diisocyanates, but he prepared a diazide by treating substituted succinic hydrazides with nitrous acid [70].

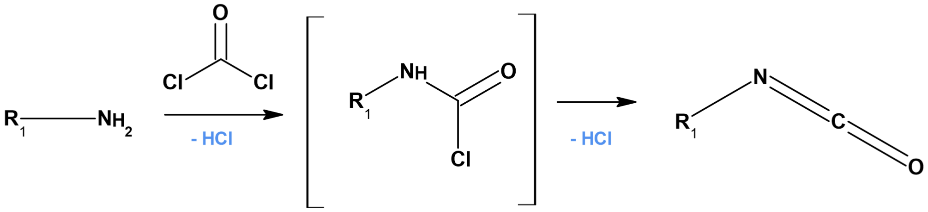


Figure 4. Preparation of isocyanate by reaction with phosgene [71].

Figure 5 shows the Curtius rearrangement mechanism in which acyl chloride derived from a carboxylic acid is treated with sodium azide to produce an acyl azide intermediate which is thermally decomposed to form an isocyanate. The isocyanate can be isolated or further reacted with various nucleophiles to give amines, carbamates, or ureases [72]. Acyl azides can alternatively be synthesized through the direct reaction of carboxylic acids with diphenylphosphoryl azide. This method has the advantage of avoiding isolation of the acyl azides, which are generally explosive [73].

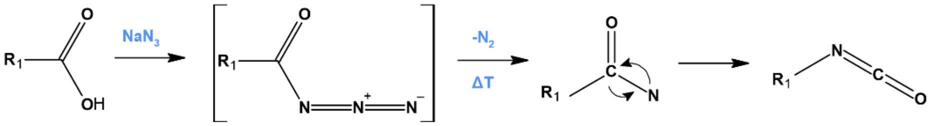


Figure 5. Mechanism of Curtius Rearrangement.

Isocyanates can also be obtained by Hofmann rearrangement (Figure 6), but this reaction often leads to undesirable by-products, such as ureas, which reduce yield and purity.

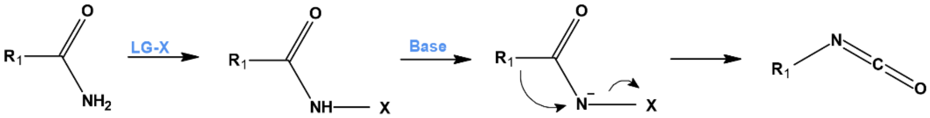


Figure 6. Mechanism of Hofmann Rearrangement.

In the Lossen rearrangement (Figure 7), the hydroxamate ester is converted to an isocyanate. In contrast, this synthesis is limited by the difficult availability of hydroxamic acids and the competing formation of self-condensation by-products [74].

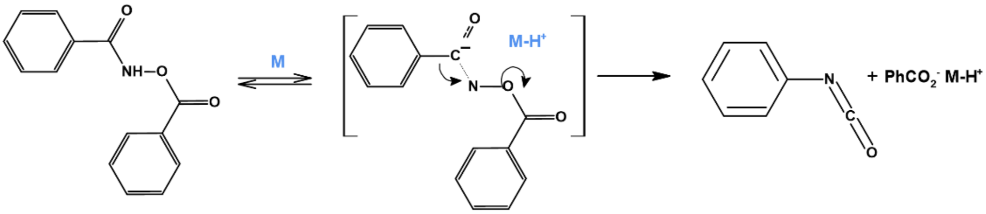


Figure 7. Mechanism of Lossen Rearrangement.

The literature discusses the use of the above methods with various reactants and reaction conditions. The most commonly described method for the synthesis of isocyanates is the Curtius rearrangement. Hojabri et al. described the preparation of a linear aliphatic diisocyanate from a fatty acid by Curtius rearrangement. Saturated diacids were prepared by ozonolysis of oleic acid to the corresponding aldehyde product. The aldehyde was then purified and oxidized to the desired acid product. The diacid chloride was then reacted with sodium azide to produce the saturated diacyl azide. The diisocyanate was then obtained by rearrangement with 68% yield and 97% purity [75].

Curtius rearrangement has also been used to obtain aromatic diisocyanates from lignin-derived phenolic acids. Syringic/vanillic acid was reacted with α,ω-dibromoalkanes in the presence of sodium hydroxide in water to give α,ω-diacids. Using a Weinstock modification of the Curtius rearrangement, the α,ω-diacids were converted to α,ω-diacyl azides. The α,ω-diacyl azides were then dissolved in dry toluene and slowly heated to 80 °C, followed by continuous heating for 8 hours to form diisocyanates by thermal Curtius rearrangement. The synthesized diisocyanates were solid, which the authors considered to pose a low inhalation risk [76].

Another publication used the Curtius rearrangement to obtain diisocyanates from succinic anhydride and isosorbide or isomannide. A two-step Curtius rearrangement was carried out with the use of sodium azide in a variety of organic solvents. It was found that the efficiency of thermal conversion of diacyl azide to diisocyanate was insensitive to temperatures in the range of 45-140 °C, but depended on the chosen solvent. Toluene was found to be the optimum solvent. The diisocyanate was obtained from isosorbide with a yield of 60%. The diisocyanates obtained had a low vapor pressure and were therefore expected to pose a minimal inhalation hazard. The use of bio-based succinic anhydride allowed the production of products with 100% green carbon content, eliminating the use of petroleum-derived reagents [77].

Curtius rearrangement was also applied to an alternative process for the production of aliphatic and aromatic isocyanates from fatty acids derived from algal biomass. In this implementation, flow chemistry was used for the preparation and conversion of intermediates, providing greater process safety. The process involves the preparation of acyl azides from hydrazines, which are then rearranged by Curtius to form isocyanates. Using flow reactions, it was possible to obtain isocyanates without isolating the explosive azides. The primary aliphatic hydrazides were found to give the highest yields. Secondary aliphatic hydrazides gave aromatic-like yields and tertiary aliphatic hydrazides gave the lowest yields. This confirms that steric effects play a significant role in the conversion to isocyanates [78].

Curtius rearrangement is considered to be one of the cleanest and most efficient methods of synthesizing isocyanates. However, its development has been limited due to safety concerns associated with the presence of inorganic azides.

An alternative to inorganic azides is the diphenylphosphoryl azide (DPPA) reaction, which provides an efficient and safe method of synthesizing isocyanates from carboxylic acids. This reaction avoids the isolation of potentially explosive inorganic azides, which greatly improves the safety of the process. Furthermore, DPPA's single-step reaction makes it more economical and efficient and DPPA itself is a stable, non-explosive liquid reactant that is easy to store and use. These properties make the DPPA method a convenient and safe approach to the synthesis of isocyanates [79, 80].

Another approach to fatty acid-based isocyanate synthesis was described by Cayli and Kusefoglu in 2008. In the first step of the synthesis, the triglyceride was brominated by reaction with N-bromosuccinimide. In the second step, the brominated product was reacted with AgNCO to convert it to isocyanate. The reaction was carried out on soybean oil triglycerides and the yield increased with increasing amounts of AgNCO. AgNCO is an expensive substance, but the by-product AgBr can be fully recovered and used to regenerate AgNCO, so the authors expect a reduction in synthesis costs [81].

Researchers have also explored an innovative approach to creating more environmentally friendly methods for synthesizing hexamethylene-1,6-

diisocyanate. They achieve this by selectively converting a renewable feedstock, methyl 2,5-dimethylenofuran dicarbamate (FDC), into hexamethylene-1,6-dicarbamate (HDC). A key challenge addressed in this work is the efficient ring-opening and deoxidation of FDC while preserving the methyl carbamate functional groups. The authors' report an optimized catalytic process for the conversion of FDC to HDC, achieving over 99.9% conversion using a 7 wt% Pt/Nb_2O_5 catalyst in a water-ethanol solvent system. This process yielded 2-hydroxy-hexamethylene-1,6-dicarbamate (HHDC) (61.0%) and HDC (12.5%). HHDC is identified as a novel compound that can either serve as a precursor for HDC or facilitate the introduction of functional groups for specialized applications. The process described contributes to the drive for sustainable HDI production, reducing dependence on fossil fuels, reducing environmental impact and aligning with global green growth strategies [82].

Until recently, the most well-known, commercially available isocyanates were Tolonate X FLO 100 and 1,5-pentamethylene diisocyanate (PDI) and its trimer. However, new alternatives to petrochemical isocyanates such as dimeryl diisocyanate (DDI), ethyl ester L-lysine diisocyanate (LDI) and isophorone diisocyanate (IPDI) have emerged over the past two to three years. The structures and green carbon content of the above bio-based isocyanates are shown in Table 2.

DDI is an aliphatic diisocyanate that can be used to produce polymers containing active hydrogen compounds. DDI is bio-based and can be used in a wide range of applications including elastomers, adhesives, sealants and coatings [83].

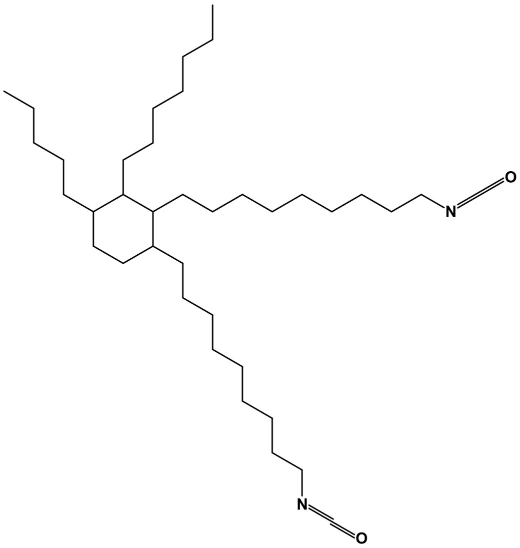
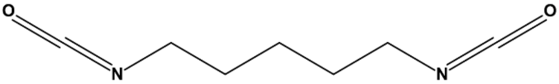
The PDI is available on the market in two versions: the aliphatic diisocyanate, marketed by Mitsui Chemicals, and the PDI trimer, marketed by Covestro. PDI synthesis involves biotechnological and chemical processes to convert starch into 1,5-pentane diamine (PDA). The product is then reacted with phosgene to produce an isocyanate. PDI is used as a curing agent for polyurethanes. It has excellent resistance to weathering, scratching and chemical treatment [84].

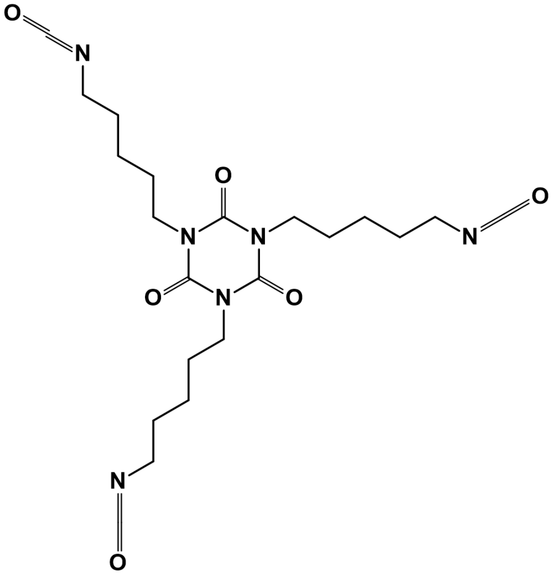
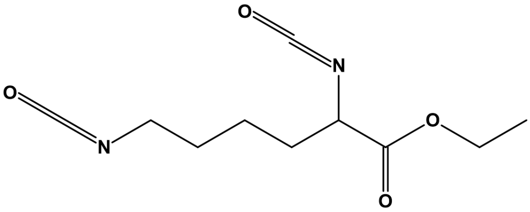
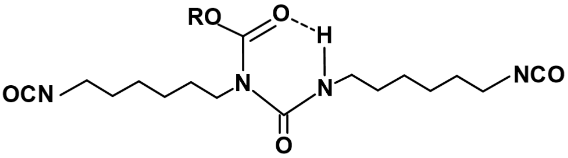
LDI is an aliphatic, asymmetric diisocyanate with an ethyl ester side chain [85]. LDI is used to make biocompatible materials, including polymers that can be used in medical applications such as implants, wound care materials, and controlled drug release systems.

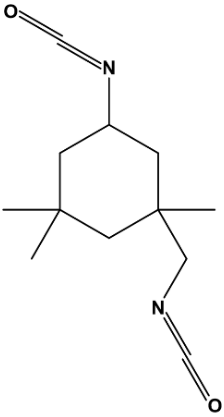
Tolonate™ X FLO 100 consists of hexamethylene isocyanate allophanate with PEG as the side chain and the biotechnology part is a palmitic acid moiety. The product is partially bio-based and has a low viscosity that is suitable for use in polyurethane coatings [86].

VESTANAT® IPDI eCO (isophorone diisocyanate) is a cycloaliphatic diisocyanate with two reactive NCO groups of different reactivity, allowing the formation of low viscosity prepolymers. According to the manufacturer, its low viscosity reduces VOCs and its methylated cyclohexane structure ensures compatibility with resins and solvents. The product is a liquid and is suitable for light stable, weather-resistant polyurethanes with good mechanical and chemical properties [87].

Table 2. Examples of commercial bio-based isocyanates, their structure, and green carbon content.

Name	Structure	Green carbon content [%]
Dimeryl Diisocyanate DDI		85.5
STABiO™ 1,5-pentamethylene diisocyanate		67 - 70

Name	Structure	Green carbon content [%]
Desmodur® CQ N 7300 PDI-trimer		70
ethyl ester L-lysine diisocyanate LDI		80
Tolonate™ X FLO 100		32

Name	Structure	Green carbon content [%]
VESTANAT® IPDI eCO		75

Moreover, less than three years ago, BASF announced a launch of Lupranat® ZERO, the first completely greenhouse gas-neutral aromatic isocyanate. Lupranat M 70 R is designed to produce MDI polyisocyanurate panels and rigid polyurethane foam in the construction industry. In addition, BASF has set itself the ambitious goal of reducing greenhouse gas emissions by 25 percent by 2030 compared with 2018 [88]. BASF emphasizes that its product is of renewable origin, but does not specify what percentage of the final product is of natural origin (therefore not included in the table above).

These examples show what has already been achieved in the field of bio-based isocyanates and highlight the importance of further development. To make significant progress in this area, both the scientific community and industry should work closely together, sharing knowledge, resources and experience to meet the challenges of sustainable development.

1.3.2. State of the art of fully bio-based polyurethanes

Although there are some reports on fully bio-based polyurethanes and their potential applications, they are still relatively few in number compared to traditional fossil-based polyurethanes. Many challenges remain in optimizing synthesis processes and finding suitable renewable raw materials that can offer comparable performance and durability to their traditional counterparts. Below are examples of scientific studies on the production of bio-based polyurethanes.

Researchers at the University of Montpellier synthesized a series of polyurethanes (PUs) using polyisocyanates and polyols with a high green carbon content. The study focused on PUs derived from the following isocyanates: L-lysine ethyl ester diisocyanate (LDI), pentamethylene diisocyanate trimer (PDI), and partially bio-based hexamethylene diisocyanate (HDI) allophanate. The polyols employed included castor oil and polypropanediol. The PUs were synthesized via two distinct approaches: a one-step reaction or a prepolymer method. The resulting thermosetting polymers exhibited glass transition temperatures ranging from -41 to +21 °C and thermal stability up to 300 °C. The green carbon content of the PUs varied between 50% and 95% [14].

Okay et al. obtained a bio-based, non-toxic polyurethane film using cellulose extracted from Luffa cylindrica and ʟ-lysine diisocyanate ethyl ester segments via step-growth polymerization. The obtained film exhibits improved hydrophobicity, thermal properties, and biodegradability [89]. In another study, biodegradable polyurethanes based on cholic acid (CA) and l-lysine ethyl diisocyanate were synthesized by growth polymerization. The effects of different monomer molar ratios on the wettability, thermal properties and biodegradability of PUR were investigated. The results showed that higher concentrations of LDI resulted in increased hydrophobicity, better thermal stability but lower biodegradability of PUR. Polyurethanes with the lowest LDI ratio degraded faster, suggesting their usefulness in biomedical applications, such as drug delivery and tissue engineering [90].

An interesting approach was taken by researchers at the University of Pittsburgh, who obtained peptide-based poly(urea-urethanes) and tested their ability to support cell growth in vitro. This polymer consisted of lysine diisocyanate and glycerol and decomposed into the non-toxic components: lysine, glycerol, and ethanol. The authors concluded that this polymer has the versatility of polyurethanes without the toxicity of other urethane degradation products and could therefore be useful in biomedical applications [91].

The effect of catalyst and NCO/OH molar ratio on bio-based polyurethane properties has also been investigated. A series of polyurethanes with and without catalysts (DBTDL) were prepared from a castor oil-based polyol and a partially bio-based aliphatic isocyanate (Tolonate X FLO 100). The PUs had various NCO/OH molar ratios including 0.9:1, 1.1:1, 1.3:1 and 1.5:1 [92]. Another researcher also used Tolonate X FLO 100 to synthesize bio-based polyurethanes, using transesterified castor oil as the polyol. The polyurethane was obtained by a one-step bulk polymerization process. The products obtained differed in the NCO/OH ratio, which was 1:1, 1.2:1 and 1.4:1. The results showed that as the NCO/OH molar ratio increased, the thermal stability of the samples and the tensile strength increased, while the elongation decreased [93].

The performance of PU coatings obtained with petrochemical HDI or PDI bio-based isocyanate (Desmodur eco N 7300) was compared in a study by Samyn et al. It was shown that the performance of both protective coatings was similar or even better when the bio-based isocyanate was used. The use of bio-based coatings resulted in shorter drying times and higher hardness. Gloss, chemical resistance, and mechanical resistance were similar. Due to better PDI hydrophobicity, the bio-based coatings had better resistance to QUV aging [94].

The use of bio-based diisocyanate DDI in the synthesis of thermoplastic polyurethanes (TPUs) has also been reported. Fully bio-based TPUs have been developed using 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, isosorbide (ISO), and 1,4-butanediol (BDO). TPUs with five different hard segment contents were obtained, ranging from 0 to 20 wt% based on the ISO content. The study showed that it is possible to replace fossil raw materials with biomass materials. The obtained materials are promising due to their properties, which can be tailored by the appropriate concentration and nature of the hard segments [51].

More et al. proposed the conversion of fatty acid derivatives into diisocyanates using a phosgene-free and environmentally friendly method. They used castor oil derivatives to synthesize two diisocyanates via a diacylhydrazide intermediate in high yield and purity. The obtained isocyanates were then reacted with commercially available fatty acid-based diols to obtain bio-based polyurethanes. The materials obtained showed semi-crystalline to amorphous behavior and good thermal stability [95].

Although fully bio-based polyurethanes offer a promising alternative to traditional fossil-based materials, their development still faces many challenges. Further improvements in synthesis processes and the search for suitable raw materials for the production of bio-based PUs with similar properties to conventional PUs remain crucial. It is also necessary to make the production of bio-polyurethanes more cost-effective and accessible to meet the growing market demand.

1.4. Summary

Bio-based polyurethanes offer a promising solution to global challenges by reducing dependence on fossil resources and minimizing environmental impact. Their synthesis relies on bio-based monomers, in particular renewable polyols and isocyanates. While significant progress has been made in the development and application of bio-based polyols, the field of naturally derived isocyanates remains under-explored and represents a critical area for future research.

The incorporation of bio-based monomers into polyurethane synthesis holds great promise for the creation of functional materials, including biodegradable foams, elastomers, and protective coatings. Furthermore, advancements in bio-based polyurethanes play a key role in reducing greenhouse gas emissions throughout the material life cycle, while promoting economic and environmental sustainability.

Isocyanates are fundamental reactants in the synthesis of polyurethanes, but their conventional production is based on the reaction of amines with toxic phosgene or its derivatives. This process raises serious environmental and safety concerns, such as the management of reaction by-products. Although compounds such as diphosgene or triphosgene (BTC) are considered safer alternatives, their use remains controversial due to associated risks [96, 97]. Although diphosgene is a liquid, its toxicity is comparable to that of phosgene. Diphosgene was originally used as a chemical weapon during the First World War. BTC is a solid at room temperature, but its vapour pressure is sufficiently high to generate toxic concentrations. Additionally, effective monitoring of these substances remains challenging. Consequently, handling diphosgene or triphosgene may be even more complex than using phosgene alone.

The development of alternative methods of isocyanate production that bypass the use of phosgene has emerged as a critical priority in future materials. This was the primary reason I explored the chemical modification of a multifunctional isocyanate and sought to synthesize bio-based isocyanates as monomers for developing innovative bio-based polyurethane materials.

Isocyanates of natural origin are an innovative group of compounds that can be derived from raw materials such as vegetable oils or fatty acids. For example, fatty acids or their derivatives can be converted into isocyanates by Curtius rearrangement. However, such bio-based monomers still face technological barriers: low reactivity, variable purity and limited availability on an industrial scale.

The polyurethane industry faces numerous challenges, including not only the development of alternative bio-based monomers, but also improving their economic and environmental performance. The industrial synthesis of bio-based monomers requires adapting the apparatus to specific reaction conditions and ensuring precise temperature control. The use of azides also presents challenges, as they are highly reactive and demand strict safety measures. Scalability and process optimization are crucial for the large-scale implementation of these technologies.

The adoption of sustainable monomer synthesis technologies has the potential to significantly decrease the environmental impact of polyurethane production while unlocking novel application possibilities for these materials. Progress in this field is essential for developing innovative materials with a minimized environmental footprint and addressing the growing global demand for sustainability. However, a number of technological and safety challenges need to be overcome before they can be synthesized on an industrial scale, particularly with regard to scaling up the process, controlling reaction conditions and optimizing production costs.

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SECTION II

AIM AND SCOPE OF THE RESEARCH

2. Aim and scope of the research work

2.1. Aim of research

The aim of this dissertation was to develop and investigate methods for the synthesis of polyurethane materials with an increased content of naturally derived raw materials. This approach is in line with the current efforts of the chemical industry to reduce the use of fossil fuels and limit carbon dioxide emissions. Special attention was given to isocyanates, a key component in polyurethane synthesis, whose innovative modifications and alternative preparation methods are of great interest to both science and industry. In particular, it focused on:

- **Synthesis and modification of bio-based isocyanates as key components in the synthesis of polyurethanes.**
- **Evaluation of the impact of the renewable raw materials used on the chemical, mechanical and thermal properties of the polyurethanes obtained.**

2.2. Scope of research

Polyurethane due to their mechanical, insulating, and chemical properties, are used in various sectors such as construction (e.g. insulating foams), automotive (e.g. flexible structural components), and medicine (e.g. biomedical materials). Isocyanates, due to their high reactivity, play a key role in the chemical industry, especially in the synthesis of polyurethanes. In the context of the increasing demand for sustainable raw materials and the reduction of the environmental impact of chemicals, the development of new environmentally friendly approaches for the synthesis of isocyanates and polyurethanes is important.

The following research objectives were accomplished in this study:

1. **Synthesis of urethane prepolymers**

Urethane prepolymers have been obtained by using a commercially available bio-based diisocyanate in which 32% of the carbon is derived from biomass. These prepolymers provided intermediates for the further synthesis of polyurethanes. The results of these studies are described in the publication *Eco-friendly ether and ester-urethane prepolymer: Structure, processing and properties*.

2. Triisocyanate modification

A modification of a commercial PDI-trimer in which 70% of the carbon was derived from biomass was carried out. The aim of this research was to increase the content of renewable feedstock in polyurethane materials while maintaining their thermal properties, with ongoing efforts to optimize their mechanical performance. These studies are presented in the publication *A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates.* This work was the basis for patent application number P.446662, which discloses the modification of a trifunctional isocyanate to produce a cast polyurethane with increased green carbon content.

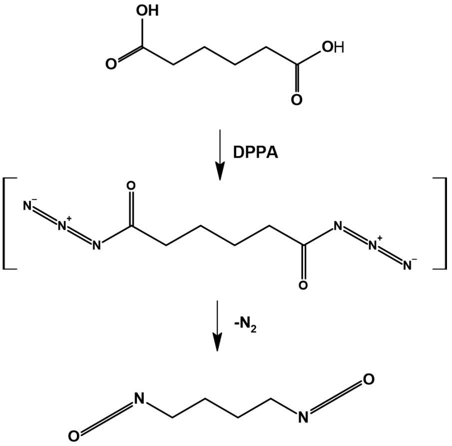
3. Phosgene-free isocyanate synthesis

A method for the phosgene-free synthesis of isocyanates using dicarboxylic acids was developed. This alternative approach makes the process safer by eliminating toxic phosgene and reduces the environmental impact by using bio-based substrates. Curtius rearrangement was used to obtain 1,4-diisocyanatobutane (BDI) and bio-based 1,8-diisocyanatooctane (ODI). Details of the synthesis are presented below, as a publication about these materials has not yet been published (submitted to a journal).

a. Synthesis of 1,4-diisocyanatobutane (BDI)

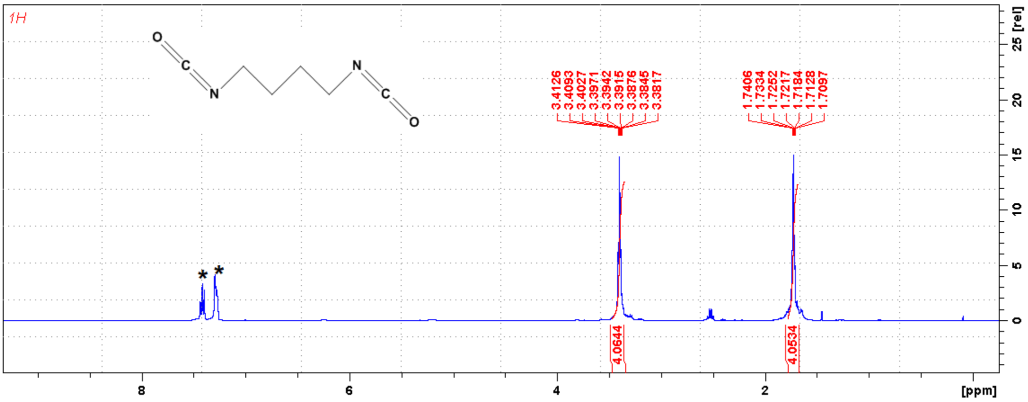
Adipic acid (20 mmol, 2.92 g) was dissolved in dry THF 50 ml under argon atmosphere and diphenyl phosphorazidate (DPPA) (44 mmol, 12.1 g).

Resulted solution was cooled to 0°C and triethyl amine (44 mmol, 6.11 ml) was added. Reaction mixture was stirred and cooled for 1 h, and additional 1h at room temperature. Solvent was removed under reduced pressure using water bath temperature <40°C. Residue was dissolved in ethyl ether (100ml) and washed with water (3 x 25ml) and brine (1 x 40ml). Solution was dried with magnesium sulfate and filtered. Volatile solvents was removed under reduced pressure and the residue was dissolved in dry toluene (30 ml). Resulted solution of hexanodioyl azide was decomposed at oil bath (100°C) through 1h. Toluene was removed under reduced pressure.



Scheme 2.1. Conversion of adipic acid to acyl azide and then acyl azide to 1,4-diisocyanatobutane via Curtius rearrangement.

NMR data: 1H NMR (CDCl3): δ 3.39 (t, 4 H, 3JHH = 6 Hz, CH2); 1.72 (quintet, 4 H, 3JHH = 3 Hz, CH2);

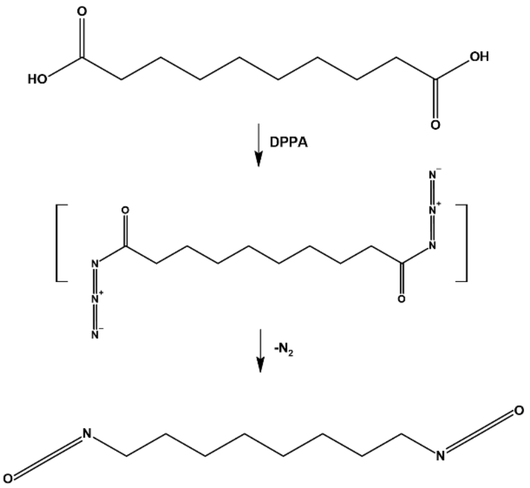


* DPPA

On the basis of ^{1}H NMR, the main product is contaminated with 17.5% DPPA although the purity was high enough for further procedures.

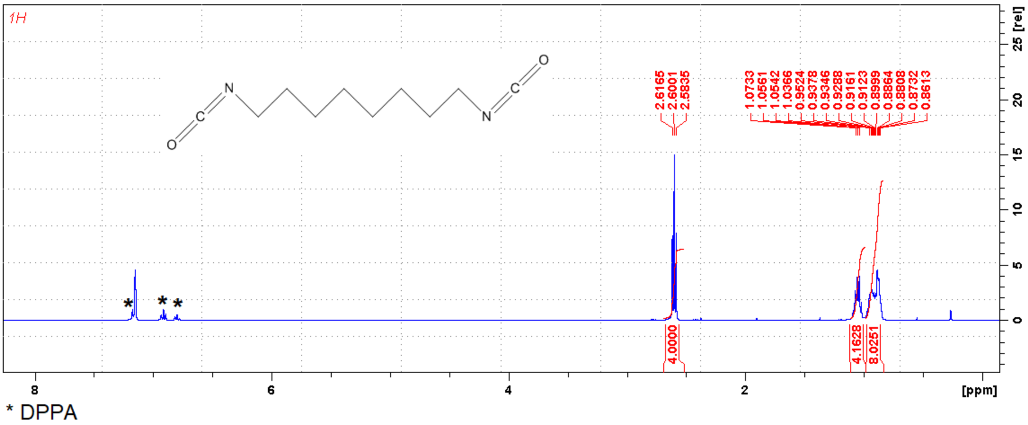
b. Synthesis of 1,8-diisocyanatooctane (ODI)

Sebacic acid (99% purity) (78 mmol, 15.93 g) was dissolved in dry THF 100ml under argon atmosphere. Resulted solution was cooled to 0°C and triethyl amine (162 mmol, 22.5 ml) was added followed by slow addition of DPPA (30’) (156.2, mmol 44.32 g). Reaction mixture was stirred and cooled for 1 h, and additional 1h at room temperature. Solvent was removed under reduced pressure using water bath temperature <40°C. Residue was dissolved in ethyl ether (100ml) and washed with water (3 x 40ml) and brine (1 x 40ml). Solution was dried with magnesium sulfate and filtered. Resulted solution of decanedioyl azide was slowly decomposed at oil bath (40°C) through 12h. Volatile solvents was removed under reduced pressure, the diisocyanate was purified by vacuum distillation.



Scheme 2.2. Conversion of sebacic acid to acyl azide and then acyl azide to 1,8-diisocyanatooctane via Curtius rearrangement.

NMR data: 1H NMR (C6D6): δ 2.46 (t, 4 H, 3JHH = 6.5 Hz, NCH2); 0.91 (quintet, 4 H, 3JHH = 6.5 Hz, CH2); 0.80-0.70 (bm, 8 H, overlapped, CH2);



On the basis of 1H NMR, main product is contaminated with 13% DPPA although the purity was high enough for further procedures.

4. Synthesis of bio-based polyurethanes

Based on the prepolymers and isocyanates obtained, bio-based polyurethanes were synthesized with green carbon contents ranging from 44% to 100%. The obtained materials were tested for their mechanical properties, thermal properties, and chemical resistance to evaluate their application potential in different industries. Part of the work has been described in the papers *The influence of bio-based monomers on the structure and thermal properties of polyurethanes* and *A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates*. Additionally, the desmodur-based materials are the subject of a patent application *P.446662*.

Polyurethanes obtained from BDI and ODI were prepared using a one-step process. The polyol was premixed with a chain extender and then the catalyst and isocyanate were added. The whole mixture was stirred for 60 seconds, degassed under vacuum for 30 seconds and then poured onto a hotplate at 60°C. After cross-linking, the samples were placed in an oven at 80°C for 24 hours. The impact of diisocyanate chain length on the polyurethane materials properties was studied based on spectroscopic and thermal measurements. Both types of bio-based polyurethanes demonstrated good phase separation. Notably, the degree of phase separation was higher in ODI-based polyurethanes, indicating a greater formation of hydrogen bonds within the urethane groups and an increased association of hard segments in ordered structures. Thermogravimetric analysis revealed a similar thermal degradation pathway for both polyurethanes, characteristic for segmented polyurethanes. However, ODI-based polyurethanes exhibited greater thermal stability, likely due to the higher molecular weight of their hard segments. Differential scanning calorimetry (DSC) results indicated the semicrystalline structure of the synthesized materials.

The research focuses on exploring the possibility of increasing the proportion of renewable raw materials in the synthesis of polyurethane materials and developing more environmentally friendly methods. The developed materials are in line with the current trend of green chemistry and enrich the existing knowledge of bio-PU. Research in this area is a contribution to the development of sustainable technologies that can have applications in a wide range of industries.

SECTION III

SCIENTIFIC PUBLICATIONS

3. Scientific outputs

	Article title	Authors	Journal
1	Challenges and recent advances in bio-based isocyanate production	Joanna Niesiobędzka Janusz Datta	GREEN CHEMISTRY IF = 9,8 MNiSW points = 200
2	Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties.	Joanna Niesiobędzka Ewa Głowińska Janusz Datta	INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES IF = 6,2 MNiSW points = 140
3	A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates.	Joanna Brzoska Joanna Smorawska Ewa Głowińska Janusz Datta	INDUSTRIAL CROPS AND PRODUCTS IF = 5,6 MNiSW points = 200
4	The influence of bio-based monomers on the structure and thermal properties of polyurethanes	Joanna Brzoska Janusz Datta Rafał Konefał Vaclav Pokorny Hynek Beneš	SCIENTIFIC REPORTS IF = 3,8 MNiSW POINTS = 140

<table>
<tr><th colspan="2">3.1. Niesiobędzka, J., & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.</th></tr>
<tr><td>Article title</td><td>Challenges and recent advances in bio-based isocyanate production</td></tr>
<tr><td>Author's contribution</td><td>My contribution was to conduct a comprehensive literature review on safer and cleaner isocyanate production methods. I was responsible for preparing the entire manuscript and am the author of all the tables and graphs in the publication.</td></tr>
<tr><td>Percentage contribution</td><td>Joanna Niesiobędzka 70%
Janusz Datta 30%</td></tr>
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Green Chemistry

CRITICAL REVIEW

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Challenges and recent advances in bio-based isocyanate production

Joanna Niesiobędzka and Janusz Datta *

Polyurethanes (PUs) are key players in the plastics industry. According to the Global Polyurethane Market (2019–2023), their value in the global market reached $95.13 billion in 2019 and is expected to grow at a compound annual growth rate of 12%. This is in line with the increase in the number of research papers and patents on the synthesis and application of petroleum-based PUs (P-PUs) and biomass or green PUs (G-PUs) (from 67 657 to 79 468, and from 198 810 to 226 164 for papers and patents, respectively, just over the past decade). Environmental concerns about fossil-based isocyanates are the reason why investigations on their green counterparts have got receiving more attention. According to statistics, almost 8% of research papers published on PUs between 2015 and the present used green-based resources. However, no comprehensive report or review dealt with such an important field in the chemistry of polyurethanes. This review highlights and reviews the production of isocyanate compounds directly from biomass. Moreover, various methods applied in the synthesis of bio-derived isocyanates are discussed. Technically, we discuss the main difficulties in the synthesis of biomass-based PUs. To address sustainability concerns, we overview the whole range of isocyanate compounds economically viable for biomass-based synthesis. We believe that the elimination of phosgene is a key to the production of green PUs. However, there is still a long way to go to develop green PUs with properties and performance comparable to fossil-based ones.

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1. Introduction

Polyurethanes (PUs) are versatile polymers widely used in a broad range of applications, such as protective coatings, adhesives and insulation, in automotive and construction industries. PUs can be found in a variety of forms,[1–3] such as solid products, foams, paints, varnishes, adhesives, and impregnations.[4] They are best known for their excellent mechanical, chemical, and physical properties, mainly abrasion resistance, durability, and tensile strength.[5,6] Thanks to promising features, the PU market has always experienced growth. Fig. 1 gives, by product, a useful view of the PU market in the United States. Accordingly, the global PU market is expected to grow at a compound annual growth rate (CAGR) of 3.8% between 2021 and 2028.[7] Estimations also suggest that urbanization and migration may result in an increase in PU consumption in the construction and transport industries. Correspondingly, the demand for PUs should taken an upward trend.

The use of fossil-based feedstocks has been seriously limited over the last few decades to avoid greenhouse gas emissions. Moreover, not surprisingly, huge amounts of plastic waste are dumped in landfills, ending up in the seas and oceans, posing a serious global crisis.[9,10] Therefore, researchers have been working to obtain greener and cleaner products. As European standard EN16575 defines, plastics derived fully or partially from biomass (*e.g.* vegetable oils, sugar, starch) are known as green materials.[11] Thus, in line with a green planet, hydrogen production, circular economy, CO_2 capture, smart building constructions, *etc.*, concerns about petroleum-based PUs (P-PUs) have increased. Fig. 2 shows the number of publications on non-isocyanate polyurethanes (NIPUs) and biomass or green PUs (G-PUs).[12,13] As can be seen, interest in this topic among researchers has been growing since 1978, but the real growth in the number of articles in this field began in the early 2000s. Since then, new articles about "greener" polyurethanes are published every year. A notable increase in interest on G-PU topics began in 2008, and on NIPU topics in 2013. Nowadays, more than 200 articles related to G-PUs and about 60 related to NIPUs are published annually. Of course, the data presented are only simplified statistics to observe a trend in the field of polyurethanes. Research papers related to the production of G-PUs or NIPUs are still relatively rare in the

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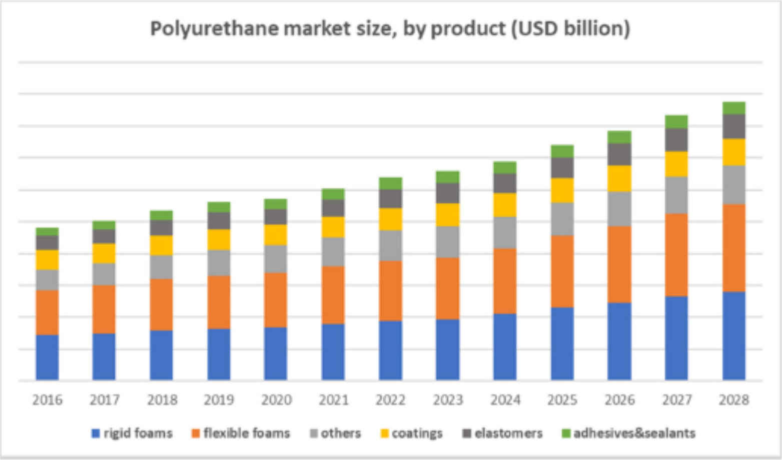


Fig. 1 Polyurethane market size based on data from the Market Analysis Report.[8]

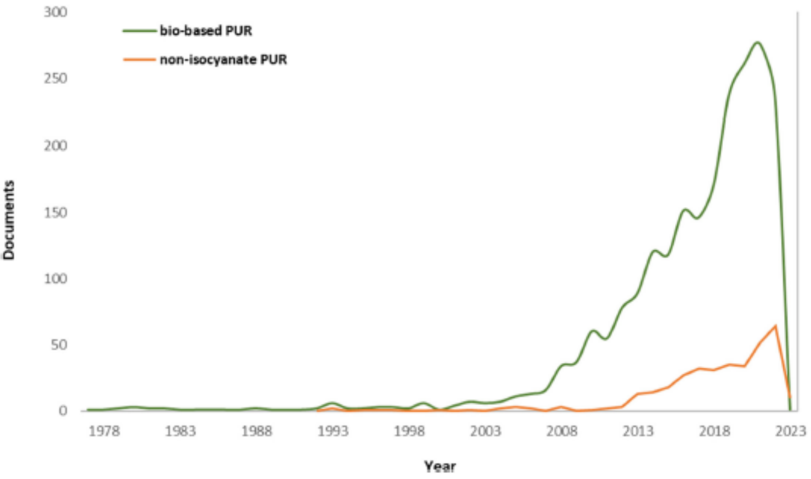


Fig. 2 The number of articles over the years.[12,13]

total number of publications on polyurethanes, therefore further development of this topic is very important.

Furthermore, a patent analysis has been conducted to confirm technological trends in the production of isocyanates. At the outset, the quantitative features of patents related to polyurethanes are examined. Fig. 3 shows the general growing trend in the field of polyurethanes and monomers for their production. The analysis was based on two keywords "polyurethane" and "isocyanate". Between 1920 and 2022, 1 442 374 patent applications for polyurethanes were registered worldwide. The increase in patent filings occurred in the 1970s. Thereafter, interest in the subject has steadily increased.

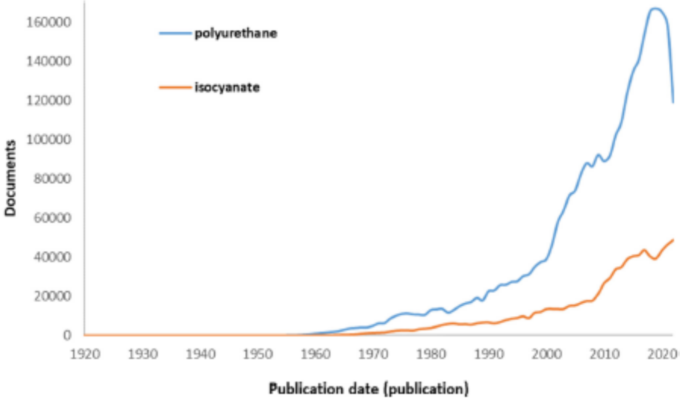


Fig. 3 Diagram of patent applications from 1920 to 2022.

Another marked increase was observed in the 2000s, and from that time the development of this topic really began. There was a slight decline in 2010, compared to 2009, which may have been caused by delays between the filing and publication of patents, as is also seen in other cases. Based on the International Patent Classification, the majority of patent applications searched in the field of "polyurethane" are layered products containing a synthetic resin (B32B27), macromolecular compounds obtained otherwise than by reactions only involving unsaturated carbon-to-carbon bonds (C08G), coating compositions, *e.g.* paints, varnishes or lacquers (C09D5), and the use of organic (C08K5) and inorganic ingredients as components of mixtures (C08K3). However, isocyanates are mainly registered in two groups: polymeric products of isocyanates or isothiocyanates (C08G18) and layered products comprising a synthetic resin (B32B27).

Typically, PUs are obtained *via* the polyaddition reaction of di- or poly-isocyanates and polyols.[14] The mechanism of the polyaddition reaction between isocyanates and polyhydroxy compounds was first introduced by Otto Bayer and coworkers in 1937.[15] This reaction can be simply explained as shown in Fig. 4.

The production of PUs is predominantly based on petroleum-based feedstocks, with benzene, toluene, ethylene, and propylene as the most common chemicals. On the other hand, raw materials based on natural products (oils, sugars, and bio-based glycerol) are used quite limitedly. Over the past two decades, the plastics industry has sought to replace P-PUs with G-PUs from renewable resources to acknowledge sustainability concerns about fossil-based resources.[15] Bio-polyols are widely known for the production of G-PUs, among them are polyols produced from rapeseed oil, soybean oil, castor oil, lignin, or

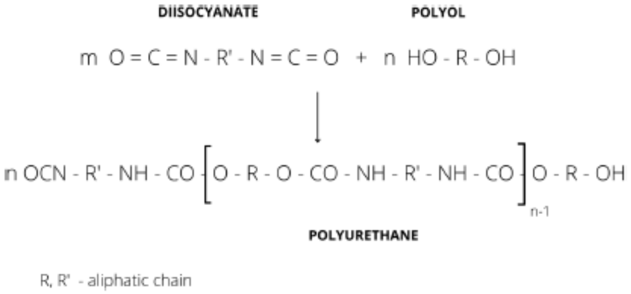


Fig. 4 Reaction scheme of diisocyanate with polyol.[16]

cardanol. Polyurethanes are often derived from chemically modified triglycerides and their fatty acids.[17] Isocyanates, on the other hand, are mainly obtained by reacting an amine with the toxic phosgene. Currently, there is a lack of comprehensive knowledge on the preparation of isocyanates from renewable raw materials. Their main drawback in addition to the toxicity of phosgene consists of limited fossil resources used to produce isocyanates.[6] Therefore, it is necessary to develop an alternative, more environmentally friendly way to produce isocyanates.[18]

In recent years, several researchers have reported the synthesis of G-PUs and measured the properties and performance of bio-based products. In this regard, some of them have also classified and reviewed the syntheses of G-PUs and green isocyanates. In recent years, several researchers have reported the synthesis of G-PUs and measured the properties and performance of bio-based products. Therefore, some of them have classified and reviewed the syntheses of G-PUs and green isocyanates. We have information on the production of both polyols and isocyanates from vegetable oils, sugars or lignin. The researchers outlined their progress in the field of bio-based isocyanates over the last few years. As a result, the potential to synthesize isocyanates also from algae or CNSL (cashew nut shell liquid) is known, and will be described later in this paper. Nevertheless, published review papers have presented some parts of this broad research field. In addition, no report or review on patents covering G-PUs has been published. Overall, three review papers published recently can be mentioned. Paraskar *et al.* also presented perspectives on the polyurethane coating industry with a focus on the use of bio-based monomers. The synthesis of polyols from vegetable oils by transesterification, epoxidation and thiol–ene coupling reactions was described in detail. However, in the review there is only a mention of the toxicity of phosgene in the production of isocyanates. The possibility of using fatty acids to synthesize bio-based isocyanates was briefly reported, and several commercially available bio-based isocyanates were mentioned. Unfortunately, this paper is weak in its detailed overview of possible routes for the synthesis of bio-based isocyanates.[19] The second paper is a summary of recent developments in the production of polyols and isocyanates based on renewable raw materials for the production of PUs. The paper presents commercially available petrochemical isocyanates, but does not deal with their toxicity and effects on human health. Moreover, this work mainly focuses on obtaining non-isocyanate polyurethanes (NIPUs), and only mentions the possibility of producing diisocyanates, for example, from dimerized fatty acids, which come from renewable resources.[19] Very recently, Ma *et al.* reported on recent advances in the synthesis of biomass-based polyols and their application in polyurethane materials. The possibilities of using such raw materials as turpentine, vegetable oils, lignin or cellulose were presented. Low price, high efficiency and reduction of pollution were pointed out as advantages of the above-mentioned materials. The paper underlines the urgency of the replacement of petrochemical polyols with bio-based polyols and reports on the research direction of bio-based PUs in the future.[20]

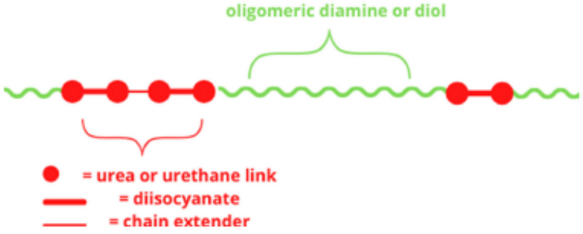
Therefore, a comprehensive review of the toxicity of commercial isocyanates as well as the classification of G-PUs seems necessary. Moreover, a patent analysis of the development of the G-PU market could shed more light on the present and future research on G-PU formulations. We comprehensively reviewed the current state of knowledge in the field of isocyanates based on renewable raw materials. In addition, the environmental impacts of fossil-based isocyanates and isocyanates derived from renewable raw materials are discussed. Furthermore, the toxicity of petrochemical-based isocyanates is systematically addressed.

The article is organized as follows: the next section provides a brief overview of polyurethanes and their trends in the global market, as well as the challenges ahead for the chemical market. The next sections include an overview of isocyanates currently used, as well as the impact of isocyanates on human health, with a focus on the toxicity of phosgene, which is used extensively in isocyanate production. Section 4 focuses on isocyanates derived from bio-based feedstocks. Specifically, it describes the possibilities of synthesizing such isocyanates, the raw materials for their production, and potential applications. It also provides a detailed patent analysis to show trends in the industry, as patents give important information about the technological trends and new technologies. Finally, future research directions and a summary of the review is included in the final section.

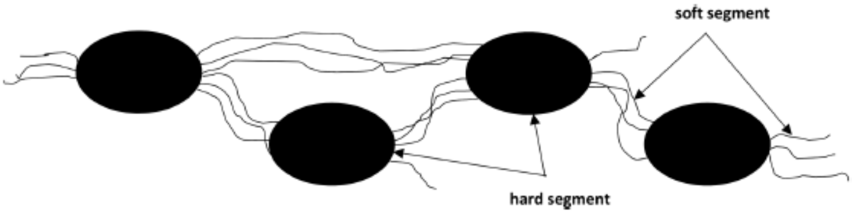
2. Characteristics of polyurethanes

The overall properties of polyurethanes are related to their chemical composition, structure, and morphology. Polyurethane, which consists of alternating hard (HS) and soft (SS) segments, is a block copolymer. A general structure of polyurethanes is shown in Scheme 1. The content of hard and soft segments affects the structure, mechanical properties, thermal stability, and low temperature capability.[21] In the temperature range from 30 to 150 °C, the hard segments are glassy (or even semi-crystalline) polymers, while the soft segments are already above the glass transition temperature. By varying the relative amounts of hard and soft phases, the physical and mechanical properties of polyurethanes can be adjusted. Increasing the content of hard segments should lead to increased modulus, strength, and brittleness of the material.[22]

Because of differences in the polarity and chemical nature of monomers between segments, domain structure formation and phase separation occur. The hard segment domains and the soft segment domains can be distinguished, as shown in Scheme 2.[23] Phase separation and domain formation depend on many factors, such as the nature of the monomers, the type and size of HS and SS, the reaction conditions, and the average molecular weight of the polyol. For example, in thermoplastic polyurethanes, the proportion of soft segments is much higher than the proportion of hard segments.[24] Consequently, these materials exhibit a complex morphology



Scheme 1 The structure of polyurethane.[22]



Scheme 2 The phase structures of segmented polyurethanes.[25]

in which flexible segments form a continuous matrix in which rigid segments are dispersed.

The microphase separation between the segments results in thermodynamic incompatibility. This incompatibility depends on several factors such as the length of the segments, the structure of the reactants, and the degree of crystallinity. Because hydrogen bonds are formed between the N–H bond of one segment and the carbonyl group of the other segment, the rigid domains act as cross-links. Therefore, the hard domains are responsible for high modulus reinforcement, while the soft segments affect plasticity and extensibility.[26]

Moreover chemistry and formulation of PUs largely affect the performance of the final product. For example, thermoplastic PUs are high-strength, lightweight materials and have relatively low processing costs. In addition, thermoplastic components are relatively easy to manufacture with high volume and precision.[27] The properties of thermoplastics can be formed by an adequate ratio of hard segments to soft segments. For example, the increase of the hard segments ratio in the molecular structure results in a better combination of matrices, which leads to higher tensile strength, better chemical resistance and higher hardness.[28] On the other hand, thermoset PUs retain their strength and shape even after heating. This makes them well suited for manufacturing durable parts and large, solid shapes.[29] For example, different diisocyanates affect the degree of swelling and thermomechanical properties of thermoset PUs. For systems based on TDI (toluene diisocyanate) and HDI (hexamethylene diisocyanate), PUs showed higher Young's modulus and lower elongation at break than for systems based on IPDI (isophorone diisocyanate). However, the type of isocyanate did not affect the thermal stability of the materials, which was good for all systems.[30]

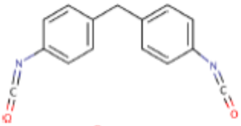
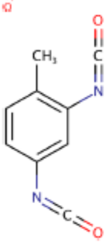
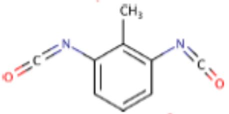
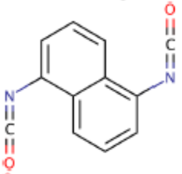
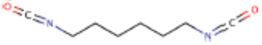
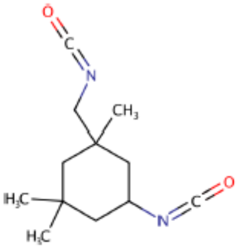
3. Fossil-based isocyanates

Commercially available isocyanates usually contain one or two isocyanate groups attached to an aromatic or aliphatic molecule. Aromatic isocyanates have some improved mechanical properties and higher reactivity, while aliphatic isocyanates do not turn yellow when exposed to light, which is a definite advantage, unfortunately they are more expensive than aromatic isocyanates.[31] In industrially produced P-PUs, two isocyanates are used in 90% of the applications: TDI (toluene diisocyanate) and MDI (diphenylmethane diisocyanate).[32] These isocyanates are produced on a large scale. TDI was the pioneer and is currently used mainly for low-density flexible foams.[33] TDI exists in two isomeric varieties; we distinguish 2,4-diisocyanatoluene and 2,6-diisocyanatoluene. TDI is obtained by hydrogenating dinitrotoluene and then reacting the product (toluenediamine) with phosgene. For commercial use, mainly a mixture containing 20% of the 2,6-isomer and 80% of the 2,4-isomer is used.[34] Unfortunately, the disadvantage of this product is the chemical inequality of the –NCO groups. The isocyanate group in position 4 may be up to 6 times more reactive than that in position 2.[35] Another important isocyanate is

MDI, which is also obtained by reacting with phosgene. MDI is generally a mixture of three isomers: 4,4′-methylene diphenyl diisocyanate (97%), 2,4′-methylene diphenyl diisocyanate (1.5 ÷ 2.5%) and 2,2′-methylene diphenyl diisocyanate (0.5%).[36] Table 1 provides a summary of commonly used isocyanates and their properties.

Fig. 5 shows the isocyanate market forecast from 2021 to 2025, the estimated growth of the sales market is 5%.[45] The increase in demand in the global market is driven by the high demand for building materials (*e.g.* adhesives and foams). Furthermore, the growth of production in the automotive industry also contributes to the increase in isocyanate sales.

Table 1 Characteristics of isocyanates[37]

Compound	Structure	Molecular weight (g mol^{-1})	Melting point [°C]	Solubility	Commercial use	Ref.
MDI		250.25	38	Benzene nitrobenzene, acetone, kerosene	P-PUs, PIR	37 and 38
2,4-TDI		174.16	20	Acetone, benzene, ethyl ether	P-PUs, PUF	39
2,6-TDI		174.16	18	Acetone, benzene	P-PUs, PUF	40
NDI		210.19	130	Water	P-PUs, curing agent	41
HDI		168.19	−55	Water	Coatings	42 and 43
IPDI		222.28	−60	Esters, ketones, ethers, aromatic and aliphatic hydrocarbons	Coatings, cross-linking, agent	37 and 44

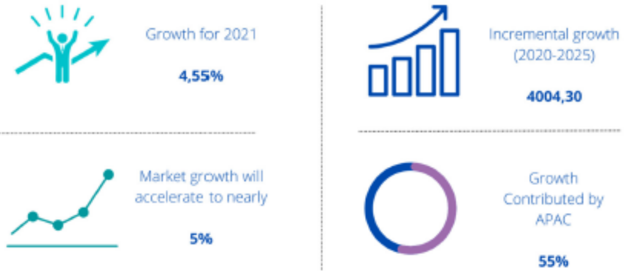


Fig. 5 Global isocyanate market 2021–2025.[45]

Due to the fact that isocyanates are an intermediate product in many applications, the demand for isocyanates is expected to expand in the next few years.[46]

The prominent players in the isocyanate market are listed below:

- Asahi Kasei Corporation,
- BASF SE,
- Bayer Material Science,
- Chemtura Corporation,
- Covestro AG,
- Dow Inc.,
- Evonik Industries AG,
- Gujarat N.V. Fertilizers,
- Huntsman Corporation,
- Kumho Mitsui Chemicals,
- Lanxess AG,
- Mitsui Chemicals Inc.,
- Tosoh Corporation,
- Wanhua Chemical Group,
- Vencorex.[45]

However, volatile raw material prices and their availability are constraints for the isocyanate market. Over and above this, the toxicity of isocyanates and their negative impact on the environment is an extremely important issue. The most economical (and therefore most widely used) way to produce isocyanates is through the reaction of phosgene with amines. Since phosgene is a highly toxic gas, this reaction is harmful to human and animal health.[47] The global phosgene market was worth $3460.35 million in 2015 to $4672.05 million by 2021, with isocyanate production consuming around 77% of global phosgene production.[48] The most significant route of exposure to phosgene is inhalation. The best way to prevent poisoning is to control exposure to hazardous levels. Unfortunately, this is difficult in the case of isocyanates because of the very low concentrations required to induce bronchospasm after sensitization. The odor threshold starts at 0.5 ppm, but toxic effects have been observed at concentrations below the threshold.[49] Animal studies suggest that exposure levels range from ≤5 ppb to 5–10 ppb.[50] In the respiratory tract, phosgene interacts with amino, hydroxyl, and sulfhydryl groups, causing the destruction of proteins and disruption of cellular functions. This results in a breakdown of the blood–air barrier and subsequent death.[51] Industries that use phosgene must have a rigorous Safety Management System. This requires companies to invest a significant amount of capital, for example, in developing hazard identification and assessment procedures and an accident prevention system. Furthermore, phosgene installation must comply with national and international agreements and regulations. The associated regulatory requirements bring additional costs and obstacles to the use of phosgene.[52] Moreover, household isocyanate contamination can also be an important problem due to the presence of isocyanates in various consumer products such as mattresses, pillows and soles. Furthermore, semi-volatile organic compounds such as isocyanates can be adsorbed by dust indoors, exposing household members to long-term exposure. Unfortunately, this problem has not been solved yet studied in depth, but there are concerns that continuous exposure to even low levels of isocyanates may influence the risk of allergy diseases.[53]

In addition, commonly used isocyanates, such as TDI or MDI, are highly toxic not only due to their method of production but also during decomposition because they release carcinogenic diamines. The most harmful route to human exposure is the inhalation of isocyanate vapors, which can cause respiratory diseases.[54] Lower molecular weight isocyanates are more volatile at room temperature, increasing the risk of inhaling their vapors. In contrast, higher molecular weight isocyanates pose a hazard when aerosolized or heated in a workplace environment. Due to the exothermic nature of the underlying reactions, inhalation risks are very common while working with isocyanates.[55] Dermal contact with isocyanates has also been shown to have negative effects on human health.[56] Their toxicity is directly related to the high reactivity of isocyanates. Exposure to isocyanates is one of the most common causes of occupational asthma in industrialized countries.[57,58] Furthermore, even low levels of isocyanates in the air can be highly toxic during inhalation. Samples of isocyanates have even been identified in wastewater after building material fires.[59] The production of isocyanates and products containing them is regulated from a health and safety perspec-

Table 2 Toxicity of isocyanates[61]

Compound	Toxicity	Ref.
Butane diisocyanate (BDI)	The degradation product is putrescine, which is a chemical compound that belongs to biogenic amines. It is formed by the breakdown of proteins. In large doses, it is toxic	62
Hexamethylene diisocyanate (HDI)	Diamines released in degradation are toxic, although less toxic than aromatic diamines from MDI or TDI	63
Isophorone diisocyanate (IPDI)	Degradation product less toxic than aromatic isocyanates	64
Lysine diisocyanate (LDI)	During degradation, LDI degrades to lysine, a nontoxic by-product	65
Methylenebis(phenyl isocyanate) (MDI)	Toxic aromatic diamine degradation products	66
Toluene diisocyanate (TDI)	Very toxic by inhalation	67

tive (Mishra *et al.*, 2009).[60] Table 2 shows the toxic degradation products of commercially used isocyanates. The above factors influence the development of bio-based isocyanates. The growth in the production of bio-based isocyanates is expected to further stimulate the demand in the market as the prices of crude oil, which is used in the production of isocyanates, are highly variable.

From research, we already know that polyurethanes based on bio-based polyols can exhibit properties similar to PUR based on petrochemical polyols. For example, Zhao *et al.* proved that TPUs based on a PLA derivative showed balanced mechanical properties, and better damping properties after multiple reprocessing.[68] Meanwhile, replacing petrochemical isocyanates with their bio-based alternatives is not so obvious, but it is feasible, this process can be implemented in various ways. One method is to synthesize PUs entirely from bio-based isocyanates, but this is rarely applied; more often a mixture of bio- and petrochemical isocyanate is used. Both solutions are economically and environmentally beneficial. When using a petrochemical isocyanate, the cost of the mixture will certainly be reduced, while using bioisocyanate, entirely or partially, will have a beneficial effect on environmental concerns. Unfortunately, bio-based isocyanates have low reactivity, which is due to their aliphatic structure.[69] However, it does not mean that their application is unfeasible. Hojabri *et al.* obtained diisocyanate from oleic acid by the Curtius rearrangement and proved its feasibility for polyurethane production by reacting with both bio- and fossil-based polyols. In their study, they found that polyurethanes based on bio-HPMDI (1,7-heptamethylene diisocyanate) had similar mechanical properties and thermal stability to HDI-based samples.[70] The same research group obtained fully bio-based PUR on HDEDI (1,16-diisocyanatohexadec-8-ene), the materials obtained had better tensile strength, but had lower Young's modulus and higher elongation than HPMDI-based PUR.[71] A group of researchers from the Netherlands also obtained PUR based on bio-isocyanate. Two isocyanates were used in this process: L-lysine diisocyanate ethyl ester (LLDI) and L-lysine tri-isocyanate ethyl ester (LLTI). The materials obtained were slightly yellow, as LLDI and LLTI were colored. Polyurethanes based on LLDI were more flexible than samples based on petrochemical isocyanate (IPDI). Unfortunately, PUs based on bio-based isocyanates swell in organic solvents, which does not happen with petrochemical PUs. In this research, PUR based on a mixture of bio-based and petrochemical isocyanates was also obtained. It has been found that the mechanical properties depend on the ratio of substrates used. The samples in which the IPDI content predominated were brittle and hard. The addition of bio-isocyanate caused the material to soften and become more fragile. On the other hand, PUs based on the LLDI/LLTI mixture showed the highest deformation at the maximum load. Meanwhile, Głowińska *et al.* studied the properties of PURs obtained from a mixture of isocyanates (Tolonate X FLO 100 (for more on this product see section 4.1), MDI and HDI).[69] The analysis showed that the type of diisocyanate mixture affects the thermomechanical properties of partially bio-TPUs. Polyurethanes based on a mixture of HDI and Tolonate X FLO 100 have higher thermal stability and show higher tensile strength than those based on a mixture of MDI.

In summary, the properties of G-PUs require further improvement. Obtaining fully bio-based PUs is expensive and more challenging than producing P-PUs. An interesting alternative is the partial replacement of petrochemical hard segments, with bio-monomers. That would certainly reduce production costs, but, unfortunately will have less environmental benefit than a full G-PU. Therefore, undertaking large-scale production of bio-based isocyanates is important from an environmental point of view. The production of fully G-PUs is expected to be an important scientific challenge at that point.

4. Bio-based isocyanates and their synthesis

In light of the restrictions on diisocyanates adopted by the European Union authorities under REACH regulation, it is extremely important to look for alternative ways to produce isocyanates or to modify the synthesis of polyurethanes.[72] The results of the patent analysis indicate a growing trend in the field of polyurethanes, while publication analysis shows increasing interest in the field of bio-isocyanates/bio-polyurethanes. The scientific results can contribute to the changes in the policy and use of isocyanates, providing information on the risks posed by various substances. A brief summary of patents related to the production of bio-based isocyanates is presented below. Patent analysis can readily identify current research gaps and can provide an important source of information for researchers. Moreover, it is a kind of science-industry connection. Later in this paper, the authors describe commercially available bio-based isocyanates and refer to papers outlining new ways to synthesize bio-isocyanates.

Table 3 shows selected patents in the field of bio-based isocyanates. Patents US9950996B2, US4749806A and CN102659631B show the synthesis of isocyanates without the use of toxic phosgene, which reduces the harmfulness of the production process itself.[73–75] Patent WO2014147142A1 discloses an allophanate composition for coating production.[76] Examples of implementation disclose an allophanate-type bio-based isocyanate prepared from hexamethylene diisocyanate. The invention EP3819259A1 relates to a process for the low-carbon synthesis of isocyanates using the RWGS reaction, providing hydrogen from water electrolysis to produce chlorine, as well as using oxygen from water electrolysis to burn polyurethane materials to form carbon dioxide and, in some cases, burning pyrolysis residues obtained from polyurethane-containing materials and using the resulting carbon dioxide as a feedstock for the RWGS reaction.[77] The carbon monoxide, advantageously produced from the recycling of the waste polyurethane material, reacts with chlorine to form phosgene, which in turn reacts with amines to form isocyanates. From isocyanates, polyurethane materials can be re-produced by reacting with polyether polyol or polyester polyol. If CO_2 and electricity from renewable energy sources are used to electro-

Table 3 Patent analysis

Patent number	Title	Brief description
US9950996B2	Bio-based aromatic diisocyanates for the preparation of polyurethanes[74]	The present invention provides bio-based aromatic diisocyanate of formula (I) (scheme included in the patent description), wherein X is OCH_3, Y is selected from —H or OCH_3, and $m = 0–12$. The present invention further provides a method for the preparation of aromatic diisocyanate of formula (I) useful for the preparation of polyurethane
US4749806A	Process for the synthesis of isocyanates and of isocyanate derivatives[75]	The present invention relates to a process for the synthesis of isocyanates and isocyanate derivatives. Isocyanates are obtained by reacting an organic halide with a metal cyanate in an organic medium in the presence of a catalyst consisting of a complex of nickel with at least one organic ligand, in which complex the nickel is in the zero oxidation state. A carbamate or a urea, respectively, are obtained by a subsequent reaction with a hydroxy compound or a primary or secondary amine. Isocyanates and their derivatives are used especially either as refined synthesis agents for the production of pesticides and medications, or as monomers or comonomers for the preparation of many macromolecular compounds
CN102659631B	One-step synthesis of ethyl isocyanate[73]	The invention relates to one-step synthesis of ethyl isocyanate. The method abandons a process of phosgene feeding in routine techniques, and uses xylene as a solvent 150–200 kg ethylamine hydrochloride is dissolved in 400–600 L xylene; the xylene solution containing 200–300 kg trichloromethyl carbonate is added into a reaction vessel in a dropwise manner in the presence of 5–10 kg of a catalyst; and the following steps are carried out: preparation of the catalyst, synthesis of the target product, separation of the target product, synthesis of ethyl isocyanate, and preparation of the product after separation. The method effectively solves the problems of high risk, severe pollution, high cost and poor quality and the like in the process of phosgene feeding in the production process in the routine techniques that use phosgene
WO2014147142A1	Allophanate composition[76]	The invention relates to a composition for preparing a coating comprising (a) at least one compound comprising at least two secondary amine functions and (b) an isocyanate component comprising at least one allophanate and at least one polyfunctional isocyanate, and optionally a solvent
EP3819259A1	Method for the production of isocyanates and polyurethanes with improved sustainability[77]	The invention relates to a method for producing isocyanates and optionally polyurethanes by the following method: synthesising phosgene from carbon monoxide and chlorine; reacting phosgene with diamines to form diisocyanates and hydrogen chloride; providing carbon dioxide gas flow; and cleaning the carbon dioxide gas flow of additional components, wherein carbon dioxide is converted by means of an RWGS reaction to form carbon monoxide and hydrogen, which are used as raw materials for polyurethane production, as well as optionally reacting the diisocyanates with polyether polyol and/or polyester polyol to form polyurethanes
CN113461894A	Sponge synthesized from bio-based isocyanate and mattress prepared from sponge[78]	The invention relates to the technical field of mattresses, in particular to a sponge synthesized from bio-based toluene diisocyanate and a mattress prepared from the sponge. Preferably, the bio-based TDI is prepared by reacting toluene extracted from organisms with nitric acid, hydrogen, carbon monoxide and oxygen

lyze water, a polyurethane material can be produced with improved sustainability. Even though the invention uses phosgene, it is an example of producing polyurethanes with a significant reduction in fossil carbon, which is in line with the sustainability policy. The last invention presented, CN113461894A, provides a sponge obtained from a bio-based isocyanate.[78] The bio-based TDI is prepared by reacting toluene extracted from organisms with nitric acid, hydrogen, carbon monoxide and oxygen. The listed applications represent only part of the state of the art in the field of sustainable isocyanate application. It can be observed that there is a correlation between current research trends and patent applications based on the results of our patent analysis.

4.1. Feedstock for the synthesis of bio-based isocyanates

Since the early days of the polyurethane industry, biomass-derived substrates have been used. Initially, rigid polyurethane foams were obtained using castor oil.[33] The development of synthetic alternatives led to the complete elimination of precursors from bio-based sources. Work on the synthesis of polyurethanes from renewable raw materials has now resumed due to predictions that fossil fuels will be depleted. Commercially produced bio-based isocyanates are already available, but their accessibility is limited. For example, Vencorex Chemicals (Saint-Priest, France) has launched an aliphatic diisocyanate called Tolonate™ X FLO 100 derived from palm oil. This isocyanate is characterized by low viscosity and 32% green carbon content.[79] This isocyanate is typically used as a precursor for the synthesis of epoxy resin for coating applications. However, to the best of our knowledge, there are no examples related to the preparation of flexible polyurethane foams using Tolonate™. Moreover, Covestro offers a PDI trimer under the trade name Desmodur® eco N 7300.[80] It is the world's first bio-based curing compound for lightweight polyurethane coating systems. It is characterized by being biobased (70%) and having a reduced carbon footprint (by 30%) compared to fossil-based products. It is used, for example, in coatings for the automotive or plastics industries. It can be used in both solvent-based and solvent-free systems. In terms of properties, it is similar to its petrochemical counterparts and has similar qualities. The last commercially available isocyanate is STABIO™ PDI, manufactured by Mitsui Chemicals.[81] It is an aliphatic polyisocyanurate based on biobased 1,5-pentamethylene diisocyanate. It is characterized by a biomass content of more than 60% and a high NCO content. It shows appropriate resistance to solvents and weathering. It is applicable *e.g.* in paints. Unfortunately, the companies listed do not disclose their formulas in patent applications, presumably they use so-called trade secrets due to the unique product. Table 4 presents a comparison of the commercially available isocyanates.

Bio-based isocyanate synthesis can be carried out by the Curtius, Hoffman or Lossen rearrangement illustrated in Fig. 6. Unfortunately, these methods have some disadvantages. The Curtius process uses highly toxic and explosive azides, while in the Hoffman and Lossen rearrangement, only aliphatic isocyanates can be obtained.[83]

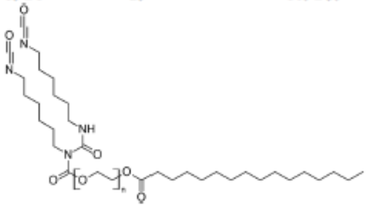
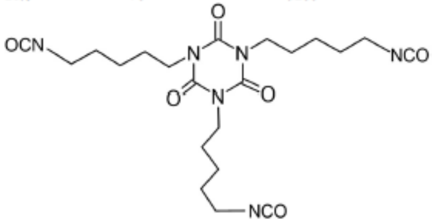
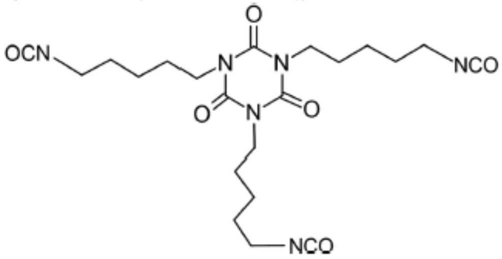
In addition to different methods of synthesis, isocyanates can also originate from different biomass components. This section provides a description of the raw materials for the synthesis of bio-based isocyanates.

4.1.1. Fatty acids. The synthesis of diisocyanates based on fatty acids was described in the second half of the twentieth century. Isocyanates obtained from vegetable oils usually have an aliphatic structure, which makes them less reactive than isocyanates derived from petrochemical feedstock with an aromatic structure.[84] In the work presented by Changqing Fu *et al.* a diisocyanate was synthesized from castor oil-derived undecylenic acid by thiol coupling (TEC) *via* the Curtius rearrangement. Diisocyanate was synthesized with a yield of 76.4%. This isocyanate was used as a starting material in the preparation of biobased polyurethane waterborne dispersion (BPUD) through reacting with castor oil and a castor oil-based carboxylic acid-type hydrophilic chain extender, which was obtained from castor oil by using 3-mercaptopropionic acid *via* TEC. Measurements showed high flexibility of the material obtained and low elongation at break. Unfortunately, the isocyanate was synthesized by the reaction with sodium azide, which is a highly explosive substance, which can lead to problems related to the expansion for large-scale production.[5]

Hojabri *et al.*[85] in their work proposed a method for obtaining aliphatic 1,7-heptamethylene diisocyanate (HPMDI) from oleic acid by the Curtius rearrangement (Scheme 3). The reaction involved the thermal decomposition of acyl azide, which was an intermediate in the preparation of isocyanates. The resulting product was then converted *in situ* to polyurethane. The problem of hydrolysis of acyl azide and isocyanate was eliminated by the use of anhydrous reagents. The obtained diisocyanate was successfully used in the next step for the synthesis of polyurethanes. The materials obtained exhibited physical properties comparable to those of similar materials based on petrochemical feedstocks. One drawback of the described diisocyanate production process is the requirement for dry reaction conditions. Moreover, the azides used are explosive and require special conditions to work at lower temperatures. Furthermore, the described method uses the solvent THF, which is a hazardous substance, so it would require further studies with the use of milder solvents. Therefore, producing isocyanates based on the described method would be difficult to implement on a large scale, and would require the development of a process and a lot of money. In a subsequent work by Hojabri *et al.*[86] the synthesized poly(ester-urethanes) obtained from polyester diols and aliphatic diisocyanates were from natural raw materials. The results obtained confirmed the structure and properties of materials based on natural products.

In another work, Hojrabi *et al.*[71] synthesized 1,16-diisocyanatohexadec-8-ene (HDEDI) from oleic acid by the Curtius rearrangement (Scheme 4). First, oleic acid was reacted with the Grubbs catalyst to give unsaturated dicarboxylic acid. In the second step, the Curtius rearrangements were carried out using ethyl chloroformate, triethylamine, and dehydrated tetrahydrofuran. Sodium azide was then added dropwise

Table 4 Comparison of bio-isocyanates

	NCO %	Biomass [%]	Viscosity [mPa s/25 °C]	Company	Ref.
Tolonate™ X FLO 100	13 ± 1 	25	140 ± 80	Vencorex	79
Desmodur® eco N 7300	21.5 	70	9200	Covestro	80
STABIO™ D-370N	25 	70	2.0	Mitsui Chemicals	82

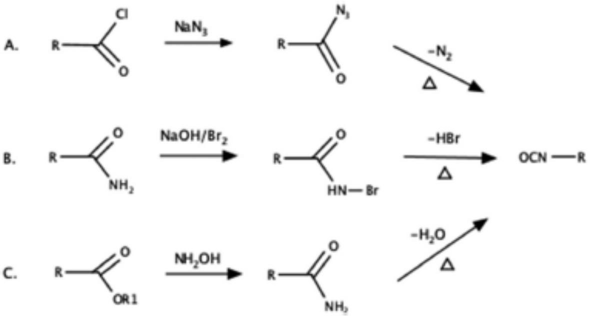
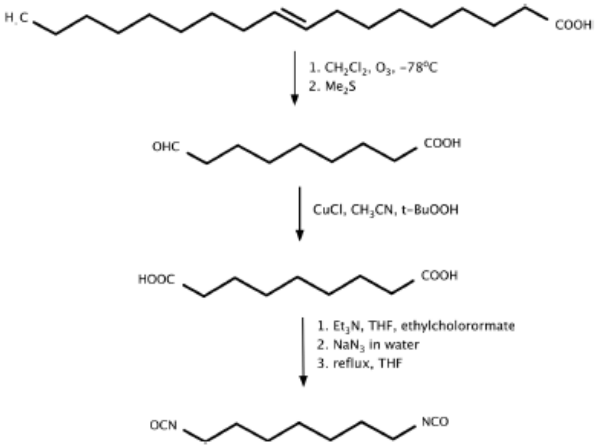
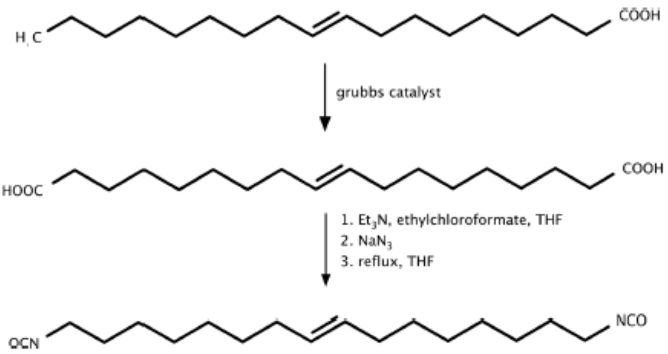


Fig. 6 Synthesis of isocyanates by rearrangement: A. Curtius, B. Hoffman, C. Lossen.



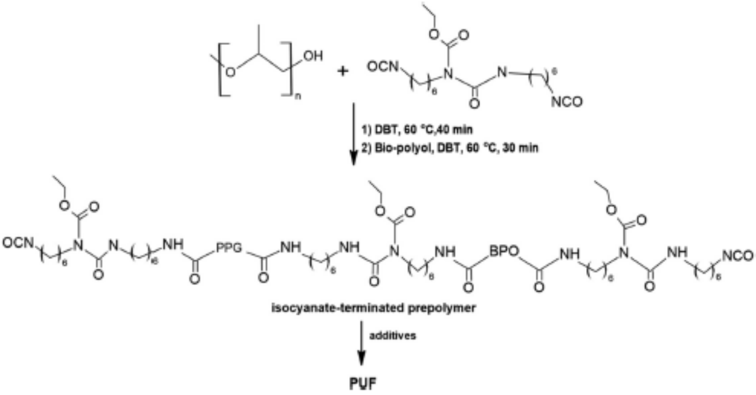
Scheme 3 Synthesis of 1,7-heptamethylene diisocyanate (HPMDI) from oleic acid by the Curtius rearrangement.



Scheme 4 Synthesis of unsaturated diisocyanates from oleic acid.

under a nitrogen atmosphere to obtain a light yellow oil, which was used to synthesize fully bio-based polyurethanes. From the study, it was found that for HDEDI-based polyurethanes, the hydrogen bond strength was higher than that of polyurethanes produced from HPMDI, which influenced their higher tensile strength at break in comparison to that of TPUs synthesized from HPMDI. In addition, polyurethanes based on HDEDI showed a lower Young's modulus and a higher elongation. Unfortunately, the melting point of HDEDI-based PUs (80 °C) and HPMDI (73 °C) was much lower than that of HDI-based polyurethanes (140 °C). Moreover, the separation of the diol from the polyol mixture required a large amount of solvent and time, so large-scale production would be impossible. The last key factor limiting large-scale production of the aforementioned isocyanates (HPMDI and HDEDI) is their reaction yields; at the laboratory scale, they were obtained with 68% and 57% yields, respectively.

Cifarelli *et al.* obtained bio-polyols from epoxidized soybean oil and linseed oil.[87] A solvent-free method using caprylic acid or 3-phenyl butyric acid with triethylamine as the catalyst was used. Then, as shown in Scheme 5, water blown polyurethane foams were prepared from the obtained bio-polyol and partially bio-based isocyanate (Tolonate X FLO 100). The G-PU foams were characterized by an open cell structure



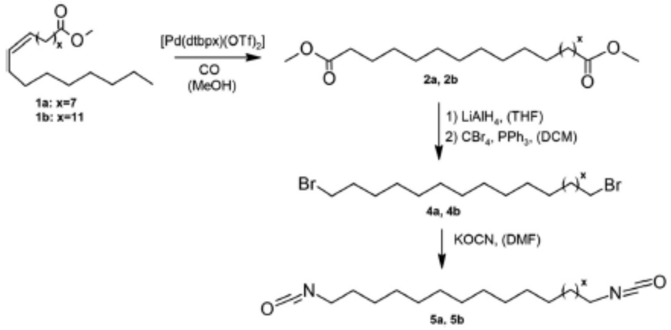
Scheme 5 Scheme of the synthesis of polyurethane foam from bio-polyol and partially bio-based isocyanate.[87]

with a well-developed pore network. The polyurethane foams obtained were characterized by slightly lower values of Young's modulus and compressive strain in comparison to those of the reference foam. Unfortunately, vegetable oil-based polyols are more flammable than petrochemical polyols.[88] As a result, the obtained foams may not be suitable for commercial applications. There are several possibilities to make such foams less flammable, *e.g.* by incorporating elements such as phosphorus or nitrogen into their backbone, however, it will cause the process to be more complicated and more expensive.

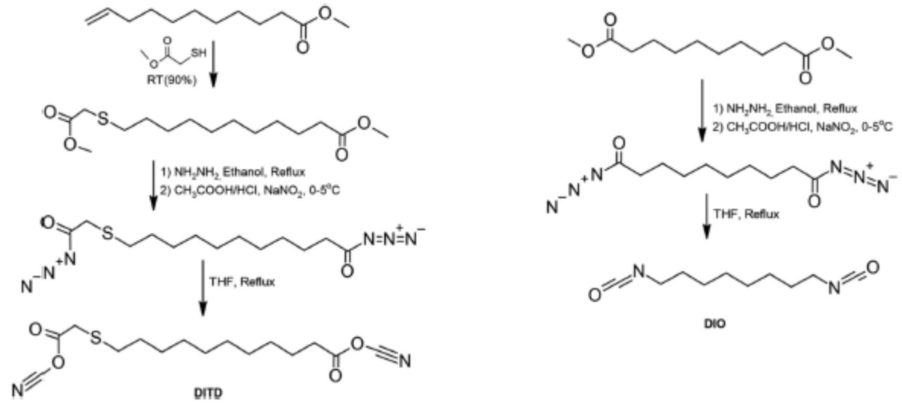
Another paper presents the synthesis of unsaturated triglycerides of vegetable oils with isocyanate groups.[89] The synthesis had several steps; in the first step, methyl oleate was brominated in the allylic position using *N*-bromosuccinimide. The crude product was purified by column chromatography on silica gel with *n*-pentane/$CHCl_3$ as the eluent. In the next step, the obtained product was dissolved in THF and portions of AgNCO were added. In both the first and the second stages, the mixture was protected from sunlight. The methyl oleate isocyanate thus obtained was mixed with methanol and refluxed overnight. Dry conditions were maintained during the synthesis. Allyl isocyanates were obtained in 60–70% yield. When dried soybean oil was used instead of methyl oleate, the by-products obtained were alkyl halides, but they reacted readily with AgNCO. Polyurethanes and polyurea were characterized by low mechanical strength and high elongation. All polyurethanes were characterized by a high swelling ratio. These polyurethanes can be used in applications where high mechanical properties are not required. Therefore, the main drawback of this synthesis was the use of an expensive reagent such as AgNCO. Due to its unique nature, it is not possible to replace it with a cheaper component. Moreover, this synthesis implies the use of solvents such as THF, therefore this synthesis has only a limited environmental benefit.

For the synthesis of diisocyanates also oleic and erucic acid esters were used. Following nucleophilic substitution, novel linear isocyanates were obtained: 1,19-diisocyanatononadecane and 1,23-diisocyanatotricosane.[90] The process consisted of four steps; in the first step, dimethyl nonadecanedioate and dimethyl tricosandioate were obtained by isomerizing alkoxycarbonylation (Scheme 6). The obtained products were then reduced to nonadecanediol and tricosanediol, which were then converted to the corresponding bromides (the Appel II reaction). In the final step, nucleophilic substitution was carried out to obtain nonadecane diisocyanate and tricosane diisocyanate. The yield of the process was up to 40%. Despite the low efficiency, this type of reaction does not cause hydrocarbon chain shortening. The diisocyanates thus synthesized were then used for the polyaddition reaction with diols. The research group successfully obtained transparent polyurethane-polyether bio-copolymers in this method. These polymers had lower melting points and reduced ductility and elasticity. To bring this method to a large scale, it would be necessary to increase the efficiency and eliminate the use of toxic solvents.

More *et al.* developed an environmentally friendly method for the preparation of isocyanates by the phosgene-free route presented in Scheme 7.[91] The substrates in the process were castor oil derivatives – sebacic acid and undecylenic acid. Both acids reacted with hydrated hydrazine, and after filtration, the solid was refluxed in ethanol and filtered to obtain a white solid. Concentrated hydrochloric acid, acetic acid, and dichloromethane were added to the prepared suspension, and then aqueous solution of sodium nitrite was dropped into the mixture. This solution in anhydrous tetrahydrofuran was then refluxed under a nitrogen atmosphere. The compound thus prepared had a yield of about 70%. DITD diisocyanate had non-equivalent NCO groups and was unstable in nature, while



Scheme 6 Synthesis of fatty acid based 1,19-diisocyanatononadecane and 1,23-diisocyanatotricosane.[90]



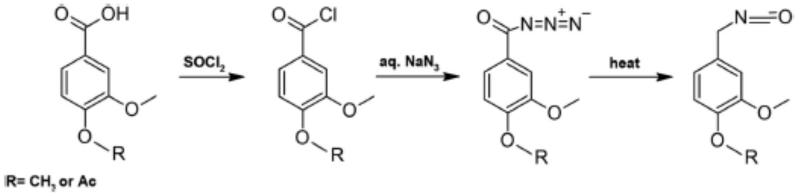
Scheme 7 Synthesis of diisocyanates based on castor oil derivatives.[91]

isocyanate with equivalent units was stable and easy to work with. Diisocyanates were used to synthesize polyurethanes with different diols. The type of monomers affected the properties of the obtained PUs, and both amorphous and semicrystalline morphologies were obtained. PUs based on DITD/propanediol were amorphous, while when the number of carbon atoms in the diol structure was increased, semi-crystallinity was induced. PUs based on DIO and linear aliphatic diol were semi-crystalline. An increase in melting point was observed when the number of methylene units increased from 3 to 4, while a decrease in melting point was caused by a higher number of methylene spacers.

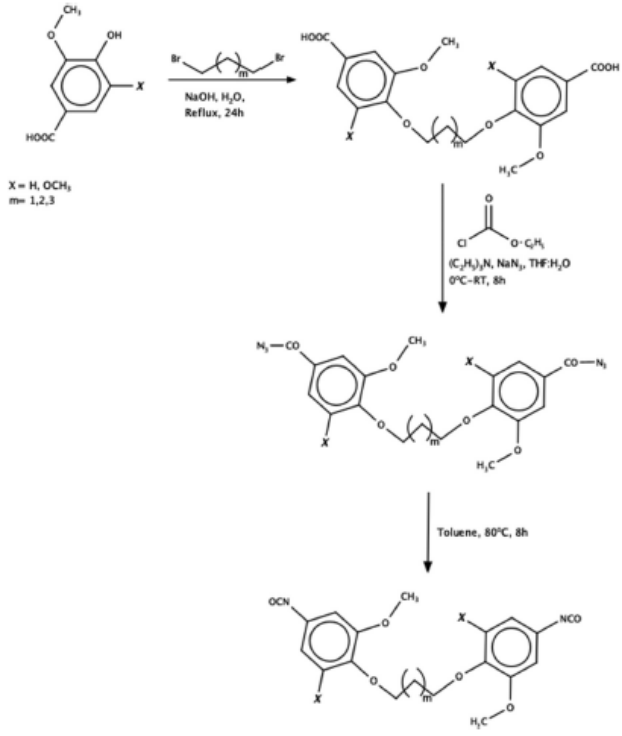
4.1.2. Lignin. Lignin is an important renewable resource due to its abundance.[92] It is an amorphous polymer obtained from hydroxycinnamic alcohols by dehydrogenation polymerization.[93] It is composed of three units: phenylpropane units (*p*-hydroxyphenyl, guaiacol and syringyl) bonded by carbon–carbon and ether bonds. Using various methods, lignin is extracted from lignocellulosic materials.[94] Processing methods and the source of extraction affect the chemical structure of lignin. Moreover, it is a by-product in many industries such as the cellulose industry, and thus its reuse is desirable. Only in 2010, 50 million tons of lignin were mined, and just 2% was used in dispersants, adhesives, surfactants, *etc.*[95] In recent years, the use of lignin-based aromatic building blocks (vanillin, syringic acid, vanillic acid, guaiacol, syringol) for the synthesis of polyurethanes has gained interest. Since lignin contains a large number of hydroxyl groups, it is often used as a substrate for renewable polyols. However, there are several studies that prove the possibility of obtaining isocyanates from lignin as well. The first reports on the synthesis of isocyanates from lignin are from 1981.[96] The paper "Lignin-Derived

Polyols, Polyisocyanates, and Polyurethanes" describes two methods for the synthesis of isocyanate from carboxylic acids. In method A shown in Scheme 8 the acid was reacted with thionyl chloride to form acyl chloride. Next, the reaction with sodium azide can occur in a non-aqueous medium ("dry method") or in an aqueous medium ("wet method"). The resulting azide is recovered from the reaction mixture and converted to an isocyanate by the Curtius rearrangement.

Kuhire *et al.* obtained in their work aromatic diisocyanates: bis(4-isocyanato-2-methoxyphenoxy)alkane and bis(4-isocyanato-2,6-dimethoxyphenoxy)alkane, synthesized by the Curtius rearrangement (Scheme 9). Vanillic acid and syringic acid,



Scheme 8 Reaction scheme for obtaining isocyanate from carboxylic acid.[96]



Scheme 9 Synthesis of aromatic diisocyanates.[97]

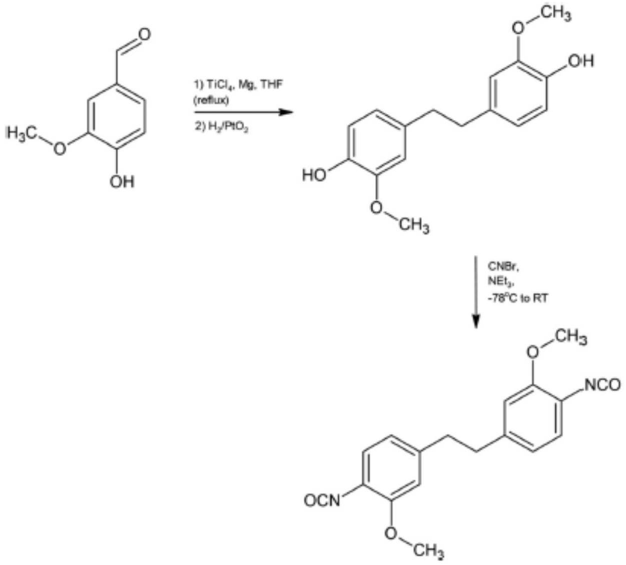
derived from lignin, were used for the synthesis. Subsequently, the obtained diisocyanates were used to synthesize poly(ether-urethanes) with aliphatic bioderived diol(1,10-decanediol and 1,12-dodecanediol).[97,98]

The direct route of synthesis by the McMurry coupling method has also been communicated. In this method, vanillin was reacted with $TiCl_4$/Mg in THF (Scheme 10). The stilbene obtained in this process then reacted with CNBr and NEt_3 to give cyanate esters. Esters were isolated by filtration and water washing. The products were obtained in appropriate yields, and their structure was studied by single crystal X-ray diffraction.[92] The prepared (bis)cyanate esters were thermally curable under mild conditions to obtain a thermosetting material, which was comparable to petroleum-derived epoxy resins.

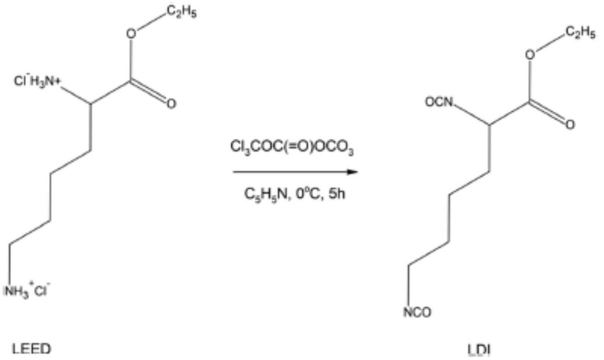
Considering the good properties of lignin, its availability, low cost and biodegradability, many attempts are currently undertaken to use it as one of the components of polymer matrices and other industrial applications.[99] However, the structure and functionality of lignin depend on its source and processing conditions. These fluctuations can affect the properties of the final product causing structure inhomogeneity. Such variations are unacceptable for commercial applications that require repeatable properties and high purity of the material.[100]

4.1.3. Amino acid-based. The vast majority of amino acid-based polyurethanes are used in medical materials. The publication 'Green Polyurethanes from Renewable Isocyanates and Biobased White Dextrins' presents methods for the synthesis of polyurethane films from biobased isocyanates. L-Lysine diisocyanate ethyl ester (LLDI), L-lysine triisocyanate ethyl ester (LLTI), and commercial isocyanate isophorone diisocyanate (IPDI) were used. Polyurethanes obtained from IPDI and bio-isocyanates were compared. IPDI-based materials were transparent and rigid, while polyurethanes obtained from LLDI were flexible and milky white in color. Unfortunately, polyurethanes (G-PUs) with LLDI tended to crack compared to polyurethanes with IPDI.[101] Likewise, Jian Han *et al.* in their work proposed a method to synthesize L-lysine diisocyanate ethyl ester and then use it to synthesize bio-polyurethane.[102] Polymerization was carried out in two steps using 1,4-butanediol and polycaprolactone diols (PCL). LDI was synthesized as shown in Scheme 11.[103]

Analysis of mechanical properties showed that the maximum tensile strength was 23 MPa and the maximum elongation was 1700%. Since PCL is a biodegradable polyester, it impacts the biodegradable properties of polyurethane. Degradation products of the obtained polyurethanes are, for *e.g.*, non-toxic L-lysine amino acids and α-hydroxylcaproic acid. However, in this method the products were obtained with a yield of 50%. Moreover, the study used pyridine, which was responsible for absorbing the chloride formed in the reaction. Before the proposed method finds industrial application, the efficiency of the reaction should be improved and the use of toxic substances like pyridine must be eliminated. It was con-



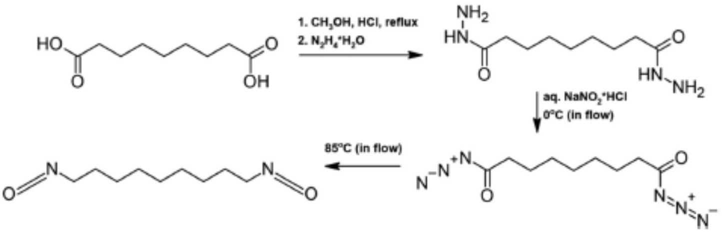
Scheme 10 Synthesis of bisphenols and cyanate esters from vanillin.[92]



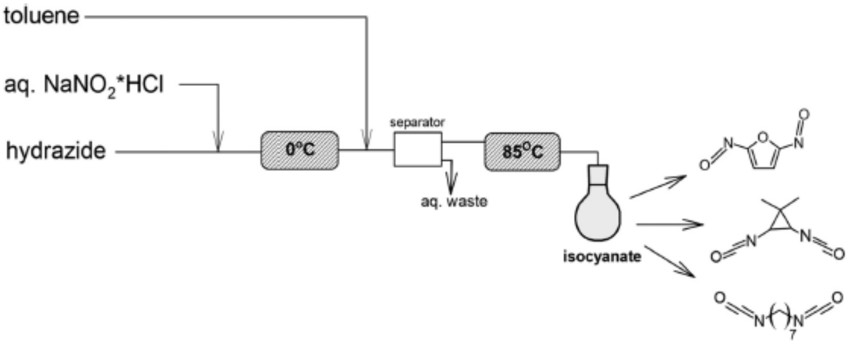
Scheme 11 Synthesis of L-lysine ethyl ester diisocyanate (LDI).[102]

cluded that this type of degradable polyurethane has potential for use in porous tubular scaffolds. In another work, a biodegradable poly(lactic acid)-poly(ethylene glycol)-poly(lactic acid) (PLA-PEG-PLA) triblock oligomer was synthesized and then, using the same stoichiometric ratio of PLA-PEG-PLA, L-lysine ethyl ester diisocyanate (LDI) and 1,4-butanediol (BDO), biodegradable polyurethanes were prepared.[104] The obtained polyurethanes exhibited rapid degradation rates and may find applications in drug delivery systems and contrast agents for magnetic resonance imaging. Also, the paper 'Non-toxic polyester urethanes based on poly(lactic acid), poly(ethylene glycol) and lysine diisocyanate' presents the synthesis of polyurethanes for medical applications.[105] The authors prepared copolymers of poly(lactic acid) and poly(ethylene glycol), followed by a chain-extension reaction with L-lysine ethyl ester diisocyanate. The polyurethanes obtained had acceptable properties.

4.1.4. Algae. The consumption of food products in chemical syntheses is disfavored by the increased demand for food. Moreover, it is also related to high agricultural land exploitation, water consumption and reduced food production. As a result, algal biomass has gained interest over the last few years. Their main advantages are fast growth rate, low habitat requirements, appropriate productivity and the possibility to produce more unsaturated fatty acids. Furthermore, microalgae residues (e.g. proteins) can be converted into polymers. Considering the aforementioned advantages, a group of researchers at the University of California developed a way to obtain isocyanates from fatty acids derived from algal biomass. The method involved the synthesis of acyl azides in a flow connected with the Curtius rearrangement (Scheme 9). This solution was applied to the preparation of aliphatic diisocyanates and then extended to the synthesis of linear alkyl or aromatic isocyanates from organic acids. Initially, the group obtained azelaic acid (AA) from palmitoleic acid derived from algae. The azelaic acid thus obtained, was then used to synthesize 1,7-heptamethylene diisocyanate (HpMDI). For this purpose, flow-through methods were employed to ensure safety and scalability. By using Fischer esterification, azelaic acid was converted to azelaic dimethyl ester and then treated with hydrazine hydrate. After the addition of nitric acid, the product was converted to azide, and toluene was added to the flow. The product thus obtained was dried and then heated in flow at 85 °C for the Curtius rearrangement (Schemes 12 and



Scheme 12 Synthesis of heptamethylene diisocyanate from algae-based azelaic acid using flow chemistry.[106]



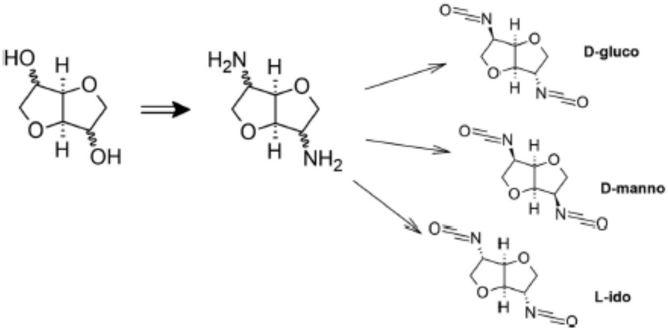
Scheme 13 Synthesis of heptamethylene diisocyanate from algae-based azelaic acid using flow chemistry.[106]

13). Diisocyanate was obtained with a yield of 80% and a rate of 500 mg h^{-1}. Environmental concerns were taken into consideration and for this a hydrazine hydrate was used, which unlike hydrazine, can be safely used. In addition, the threat of instability of the high-energy acyl azide was eliminated by using flow chemistry.

To the authors' best knowledge, the presented papers are the only reports on the synthesis of isocyanates from algae. These methods may be a promising way to synthesize bio-based isocyanates in an environmentally and economically friendly way. Among the major challenges of algal production is identifying strains with high lipid content, growth rates and high lipid yields for large-scale production.

4.1.5. Saccharides. Natural sugars are abundantly available due to the fact that sugar biomass is extracted from corn, soybean, and wheat among others. They have many benefits like structural diversity, being harmless to human health, hydrophilic character and less environmental impact as compared to petroleum based substances. Substrates for polymer production can be obtained from sugars like mannose, lactose or galactose.[107–109]

Bifunctional dianhydrohexytols can be obtained from polysaccharides. They are obtained from renewable resources, such as by double dehydration of D-glucose.[110,111] Bachmann *et al.* used dianhydrohexitols with three configurations (D-gluco, L-ido, D-manno) to prepare diisocyanates (Scheme 14).[112] Two methods, cold and hot phosgenation, were used to convert the substrates into diisocyanates. The yield of the process depended on the stereochemistry of the dianhydrohexitols. Phosgene addition was more efficient when the amino groups were orientated out of the molecular plane. Therefore, the synthesis of diisocyanate with an L-ido configuration gave the highest yield. The obtained diisocyanates were then used in a polyaddition reaction to obtain new polyurethanes. The advantage of such an isocyanate will be the use of natural raw materials as substrates, however, the authors should consider using a synthesis method other than phosgenation.



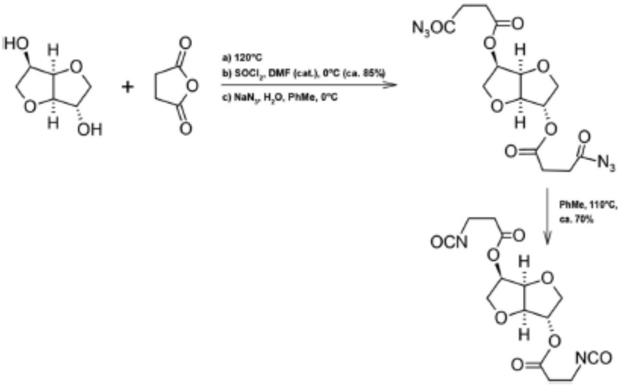
Scheme 14 Monomer synthesis.[112]

An interesting substitute for petroleum-based substances is isosorbide, due to its rigidity and thermal stability. Zenner *et al.* obtained diisocyanates based on isosorbide. In the synthesis, succinic anhydride was also used because of the competitive price of production of succinic acid and the ability to eliminate petrochemical reagents.[113] As shown in Scheme 15 in the first step of the reaction isosorbide and succinic anhydride were reacted by double esterification under solvent-free conditions. Then the Curtius rearrangement was used to obtain the product, thionyl chloride and sodium azide were used for this step. Unfortunately, aromatic solvents such as toluene were used in this synthesis. The yield of the process to obtain diisocyanate from isosorbide was 60% in total, it is possible to increase the yield to 70% by obtaining isocyanate directly from diacyl azide. The diisocyanates thus obtained were successfully applied in the synthesis of thermoplastic polyurethanes.

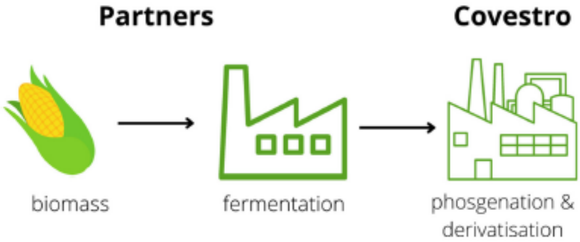
Starch derived from field corn (non-edible) was used by Covestro to develop aliphatic pentamethylene isocyanate (PDI). It is the first commercial diisocyanate that contains 70% renewable carbon content. Scheme 16 illustrates the production process of this isocyanate.[114]

4.1.6. Cashew nut shell liquid (CNSL). Phenols, hemicellulose, and other wood-derived compounds can be suitable starting materials for chemical synthesis due to the fact that they are not competitive with the food industry (they are classified as non-edible biosources). This monomer source can be cashew nut shell liquid, which belongs to natural phenols. CNSL is a by-product of cashew nut kernel removal and may be an interesting renewable resource.[115] There are various components in CNSL, the main ones being anacardic acid, cardanol, cardol, and 2-methylcardol. Cardanol can be used in the chemical industry for coatings, resins or surfactants.[116]

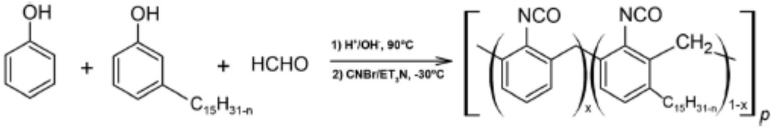
Novolac resins that contain cardanol can be converted to the corresponding cyanate esters. Nair *et al.* in their work investigated the synthesis of cardanol-modified novolac resins and the effect of cardanol on their thermal stability (Scheme 17). The cyanate esters formed thermally stable



Scheme 15 Synthesis of diisocyanate.[113]



Scheme 16 Industrial procedure for Desmodur eco N7300 from Covestro.[114]



Scheme 17 Synthesis of cardanol-based cyanate ester resins.[116]

phenol-triazine networks after curing.[117] However, increasing the cardanol content decreased the thermal stability of the cured polymers. While Kulkarni *et al.* synthesized cyanate ester monomers containing pentadecyl-substituted cyclohexyl moieties.[118] The obtained compounds, 1,1-bis(4-cyanatophenyl) 3-pentadecylcyclohexane, as well as 1,1-bis(4-cyanatophenyl) cyclohexane were characterized by Fourier-transform infrared spectroscopy and proton-nuclear magnetic resonance, among others. These compounds exhibited better processability, lower melting point and lower onset of cure compared to commercially available cyanate esters.

5. Conclusions and future perspectives

This article presents up-to-date information about biomass-derived raw materials for isocyanate production. In recent years, increased interest in the topic of bio-based feedstocks has been reported. Bio-based raw materials used in the synthesis can include vegetable oils, lignin or amino acids. The isocyanates produced from biomass are characterized by a high green carbon content and low CO_2 emissions. Moreover, the use of biomass provides an alternative to depleting fossil fuel resources. Monomers of biological origin are currently not used on a large scale, mainly for financial reasons, but, as can be seen, the environmental costs are much lower than those of petrochemical raw materials. In addition, the toxicity of isocyanates of petrochemical origin and the phosgene used in isocyanate production were discussed. Many review papers have considered the synthesis of polyols from feedstock of natural origin, but limited information is present for the synthesis of bio-based isocyanates. This review analyzes both patent applications and papers related to sustainability in isocyanate production. Among the factors slowing the development of bio-based polyurethanes are high production costs and limited production of commercially available monomers. The authors believe that long-term efforts are required to achieve a sustainable and environmentally friendly way of producing polyurethanes. These include improving technology to produce biobased monomers on a large scale at low cost, and developing new biobased monomers. Researchers should also emphasize on accelerating the commercialization of existing bio-based monomers. Ongoing development of sustainability policies and consumer awareness is also extremely important. Therefore, this paper presents the advantages and disadvantages of currently known methods of isocyanate production. Each of them has its own critical points that should be considered before large-scale production. Several of the outlined methods seem to be interesting alternatives to petrochemical isocyanates. Certainly, the transition from petrochemical substrates to renewable feedstocks will be a major success for the environment and industry. Perhaps a good alternative in the beginning would be to produce PUR from a mixture of isocyanates to reduce the cost while on the other hand increasing the green carbon content of the product, without sacrificing properties. It is believed that this review will be beneficial for researchers, academics or any other industry professionals seeking alternatives to commercially used isocyanates of petrochemical origin. The authors express hope for further development in this direction.

Conflicts of interest

There are no conflicts to declare.

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Co-authors’ statements of contribution

Gdańsk, 07.03.2025 r.

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DECLARATION

As a co-author of the following publications:

1. Niesiobędzka, J., & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.

2. Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.

3. Brzoska, J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.

4. Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of providing consultation during the execution of the experimental work, evaluating the literature review, and proofreading the papers. Therefore, my contribution to the above-mentioned publications is as follows:

1. 30%

2. 15%

3. 15%

4. 10%

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Date and signature

3.2. Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.	
Article title	Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties
Author's contribution	I was responsible for preparing part of the manuscript. I co-led the syntheses of the materials and was partially responsible for their analysis. Additionally, I prepared the graphs and wrote the description of some of the research results (NMR, rheology).
Percentage contribution	**Joanna Niesiobędzka** **50%** Ewa Głowińska 35% Janusz Datta 15%

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Article

Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties

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Abstract: This study concerns bio-based urethane prepolymers. The relationship between the chemical structure and the thermal and processing parameters of bio-based isocyanate-terminated ether and ester-urethane prepolymers was investigated. Bio-based prepolymers were obtained with the use of bio-monomers such as bio-based diisocyanate, bio-based polyether polyol or polyester polyols. In addition to their composition, the bio-based prepolymers were different in the content of iso-cyanate groups content (ca. 6 and 8%). The process of pre-polymerization and the obtained bio-based prepolymers were analyzed by determining the content of unreacted NCO groups, Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, thermogravimetry, and rheological measurements. The research conducted facilitated the evaluation of the properties and processability of urethane prepolymers based on natural components. The results indicate that a significant impact on the processability has the origin the polyol ingredient as well as the NCO content. The thermal stability of all of the prepolymers is similar. A prepolymer based on a poly-ether polyol is characterized by a lower viscosity at a lower temperature than the prepolymer based on a polyester polyol. The viscosity value depends on the NCO content.

Keywords: ether-urethane prepolymer; ester-urethane prepolymer; bio-based diisocyanate; chemical structure; thermal analysis; processing properties

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1. Introduction

For the first time, Bayer obtained polyurethanes in 1947 and since then the interest in them has been growing steadily [1,2]. Chemical industry products, including polyurethanes, help to reduce energy costs and the negative environmental impact of the industry. Plastics-made car parts significantly reduce vehicle weight, which has a positive effect on fuel consumption. This improvement has been estimated at around 7% for every 10% reduction in vehicle weight. Moreover, a report from the American Chemistry Council shows that the use of appropriate polymer materials in buildings can save 40 times the energy used to produce it. It was also found that over the years plastics and insulation materials have helped to save 467.2 trillion BTU (BTU—British thermal unit) [3].

Polyurethanes can be a beneficial and safe way to reduce carbon dioxide emissions and the effects of global warming. The demand for these plastics is steadily increasing due to reduced production losses, increased recyclability, and the extended life cycle of the end product caused by advancements in polyurethanes materials manufacturing technology.

Federal governments and agencies are increasingly concerned about the harmful health effects of isocyanates used in polyurethane production. In addition, the production of polyols, which are the second essential component of plastics, depends on the availability of fossil fuels. Their production process is also environmentally harmful. Consequently, the polyurethane industry is constantly striving to sustainably develop its business practices. According to the Global Risks Report prepared in 2020, an unstable geopolitical situation in oil extraction regions contributed to a price shock, which additionally translated into instability on the dependent market of raw materials [4]. Over the past year, oil prices have risen by 158.71% on the stock market [5]. By comparison, the price of corn (the input for bio-glycols production), which can be processed into raw materials necessary for the production of polyurethanes, has increased by 60.75% [6]. Such price fluctuations make natural resources a more stable source for the production of urethane monomers. Moreover, for the first time in 2019, among the members of the World Economic Forum community, environmental concerns dominated the top long-term risks by likelihood of occurrence. Among the top global risks were listed: failure of climate change mitigation and adaptation by government and business, and human-made environmental damage and disasters [4]. Due to the above mentioned aspects, it is important to develop substrates from natural resources for use in polyurethane production.

Polyurethanes can be obtained by a two-step method which involves the use of prepolymers [7]. In the first step, the polyol reacts with a moderate excess of the diisocyanate relative to the hydroxyl groups of the polyol. The isocyanate is attached to the end groups of the polyol to form a product containing terminated isocyanate groups and an excess of diisocyanate. The resulting prepolymer contains a certain percentage of free isocyanate groups, on the basis of which the amount of the chain extender to be added is calculated. In the second step, the prepolymer is reacted with a predetermined amount of the chain extender in the presence of a catalyst [8].

The use of excess isocyanate is required to prevent the increase in molecular weight caused by the chain length increase in the unreacted polyol, reacting with the prepolymer with free isocyanate groups. Prepolymers in which excess isocyanate remains in the product are called "quasi-prepolymer". In practice, this term refers to materials with high levels of unreacted isocyanate (>12%), while the term "prepolymer" is used for low levels of unbound isocyanate (<12%).

Among the numerous advantages of prepolymers, particular attention should be paid to their stability during storage and ease of processing because of their aggregate state (liquid). Furthermore, the prepolymer ensures better compatibility with additional components of the mixture and allows for a more homogeneous structure of the final product than those obtained in one-step synthesis [9]. A very important advantage of prepolymers is the ability to pre-build the properties of the polymer. A number of these advantages influence the high demand for prepolymers, which is approximately 500 million pounds per year for commercial applications [10]. Isocyanate-terminated urethane prepolymers are the intermediate in the polyurethane preparation with the prepolymers method, and can be processed with industrial grade machines. Based on previous studies, it was found that prepolymers containing 6 to 8% unreacted NCO groups have high application potential due to their viscosity. Kasprzyk et al. proved that an increase in the content of unreacted NCO groups contributes to an increase in the degree of phase separation, because of the higher content of hydrogen bonds between urethane-urethane groups. It was also found that the materials obtained from the prepolymer containing 8.0% of unreacted NCO groups showed the highest content of rigid segments. The content of rigid segments affects the value of tensile strength and Young's modulus [11].

In industrial processes, one of the most important processing properties of polyurethanes is their rheological behavior of components. Rheological measurements allow for determination of the viscosity of fluids under specific conditions of pressure and temperature. Rheological behavior and viscosity are also related to the structure of polymer chains [12].

Rheological property studies are important for:

- designing pipelines, processing equipment, pumps, etc.;
- the quality control of intermediate and end products;
- the analysis of properties of substances during their use.

In developed countries, the total amount of processed polyurethanes is several million tons. Therefore, even small improvements to processing properties result in positive economic changes. Research on rheological measurements is also essential in terms of industrial modernization and increasing demand for high quality of end products.

Current scientific work focuses on transforming industry to become more ecological, e.g., by using raw materials of biological origin [13]. According to European standard EN16575, bio-based products are defined as partially or completely derived from biomass. They are important elements of the implementation of the bio-economy, in which products of biological origin replace those of the mining industry. The bio-economy sector, located only in the European Union, is estimated to generate a turnover of EUR 2.1 billion and create jobs for more than 18 million people [14]. Fossil fuel mining can pose a threat to the environment, so effective measures to minimize negative environmental impacts are now a priority for future generations. An additional problem related to the extractive industry is growing prices of petroleum products and their limited resources [15]. Thus, the use of renewable raw materials that are available and relatively inexpensive is a desired alternative. The benefits of processing bio-monomers are also an important advantage of natural raw materials, they reduce energy consumption by lowering the activation energy of polyurethane processing [12].

Due to the considerable interest in materials of natural origin and the policy of sustainable development, it is expected that there will be an increase in the production of bio-monomers as components in the synthesis of polyurethane materials. Bio-monomers for the polyurethane industry are produced from plant biomass. There are several manufacturers in the market offering commercially available biopolyols. One of them is Velvetol produced by Allessa [16] or PriplastTM 3238 offered by Croda [17]. The market of commercially available bio-isocyanates, however, is poorer than the market of bio-polyols. There are three major producers of bio-isocyanates. One of them is Covestro, which offers a PDI trimer under the trade name Desmodur® eco N 7300 [18]. Mitsui Chemicals offers bio-diisocyanate under the trade name STABIO™ PDI [19]. Another manufacturer of bio-isocyanates is Vencorex, which offers Tolonate™ X FLO 100 [20].

In the present study, the structure-property relationships of novel bio-based urethane prepolymers prepared with bio-monomers were investigated. We studied the correlation between chemical structure of the obtained bio-based urethane prepolymers and their thermal and rheological properties. To the best of our knowledge, there is no detailed publication on the thermal properties of prepolymers derived from bio-based raw materials.

2. Materials and Methods

2.1. Materials

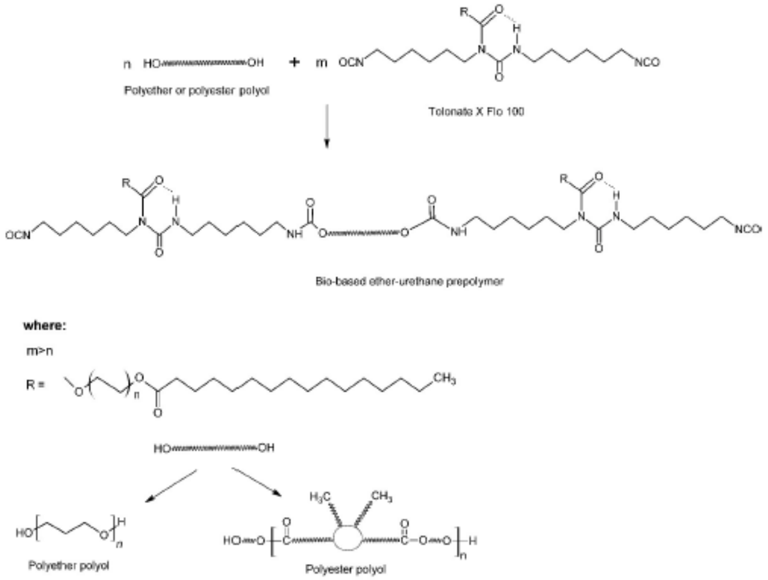
In the synthesis of prepolymers based on renewable raw materials we used aliphatic isocyanate Tolonate X FLO 100 provided by Vencorex (Saint-Priest, France), two types of polyols: PRIPLAST 3294^{TM} (Priplast) semicrystalline polyester bio-polyol supplied by Croda (Snaith, UK) and Velvetol H2400 (PO3G) polyether bio-polyol supplied by Allessa GmbH (Frankfurt, Germany). The reaction inhibitor was orthophosphoric acid supplied by POCH Gliwice (Gliwice, Poland).

2.2. Prepolymer Preparation

The research involved obtaining ether-urethane and ester-urethane prepolymers with ca. 6% and 8% unreacted NCO content. The reactor placed in the heating jacket was filled with polyol. A thermometer and a mechanical stirrer were placed in the lid of the reactor. Initially, the polyol was heated to 60 °C and then degassed under vacuum at 90–95 °C for 1.5 h. In the next step, the mixture was cooled to 60 °C and the isocyanate and the reaction inhibitor were added. The inhibitor was used because it inhibits the formation of cross-linking bonds to prevent excessive increase in the viscosity of the prepolymer. The synthesis was carried out at the temperature of 85 °C for another two hours. A scheme of laboratory apparatus for the synthesis of urethane prepolymers is included in the Supplementary Materials as Figure S1. During the reaction, the percentages of NCO groups were determined by titration according to ISO 14896:2010. Table 1 shows the actual amounts of free isocyanate groups measured after the two-hour reaction time. Scheme 1 shows the overall ether and ester-urethane synthesis method. The structure of Tolonate X FLO 100 in the Scheme 1 was adopted from [21].

Table 1. NCO content.

Composition of Sample	Calculated Percentage of Unreacted-NCO Groups	Sample Code	Determined Percentage of Unreacted Isocyanate Groups [%]
Tolonate X FLO + Velvetol H2400	6%	PRE_PO3G_6	5.22 ± 0.03
Tolonate X FLO + PRIPLAST 3294TM	6%	PRE_PRIPL_6	5.51 ± 0.14
Tolonate X FLO + Velvetol H2400	8%	PRE_PO3G_8	7.28 ± 0.03
Tolonate X FLO + PRIPLAST 3294TM	8%	PRE_PRIPL_8	8.42 ± 0.08



Scheme 1. Reaction scheme for ether- and ester-urethane prepolymers formation.

2.3. *Characterization*

2.3.1. Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectra of the polyether urethane prepolymers, polyester urethane prepolymers, and monomers were obtained with a Nicolet 8700 spectrophotometer. The spectra were recorded after 64 scans in a wavenumber range from 4500 to 500 cm^{-1} with a resolution of 4 cm^{-1} in absorbance mode.

2.3.2. ^{1}H NMR

Proton nuclear magnetic resonance (^{1}H NMR) spectra of the prepared bio-based prepolymers were obtained with the use of a Bruker spectrometer. The operating frequency was 400 MHz for protons. The ca. 10% *w*/*v* solutions of the prepolymers and polyols were prepared in a DMSO-d_6 solvent at ambient temperature. The simulation and iteration of the spectra were carried out using Bruker Avance III HD TopSpin software v.4, number of scans (ns): 16; delays (D1): 1 s, (D16): 0.0002 s.

2.3.3. Rheological Measurement

Rheological tests were carried out using a Brookfield R/S+CPS rheometer with a cone-plate geometry (C50-2 cone). Prepolymers obtained from ether polyol and ester polyol containing ca. 6% or 8% of free isocyanate groups were tested. The samples were tested at the following temperatures: 60 °C, 70 °C and 80 °C. Measurements were made at a fixed and controlled shear rate using Rheo3000 software version 1.2.1377.1.

The following program was applied:

- increasing shear rate from 0 to 300 s^{-1} in 120 s,
- constant shear rate of 300 s^{-1} for 120 s,
- decreasing shear rate from 300 to 0 s^{-1} in 120 s.

Rheological models were proposed that best describe the rheological behavior of fluids. The three most commonly used models were distinguished: Newton's, Herschel-Bulkley's, and Ostwald-de Waele's. They are characterized below.

The Herschel-Bulkley model is the simplest model of flow curves of nonlinear plastic-viscous fluids. The model is expressed in the Equation (1):

$$y = k_1 + k_2 x^{k_3} \tag{1}$$

The Newton model is characterized by ideal fluids that show a linear relationship between the shear stress and shear rate. This model is described by the Equation (2):

$$y = k_2 x \tag{2}$$

Ostwald-de Waele describes shear-thinning fluids without a yield point. This model is expressed in the Equation (3):

$$y = k_2 x^{k_3} \tag{3}$$

where:

x—shear rate [s^{-1}]
y—shear stress [Pa]
k_1—yield stress [Pa]
k_2—consistency index [-]
k_3—flow behavior index [-]

2.3.4. Thermogravimetry (TGA)

The analysis of monomers and prepolymers was performed using a Perkin Elmer TGA Pyris 1. The test was carried out in the temperature range of 50–600 °C under nitrogen atmosphere flow rate of 20 mL/min, for samples weighing up to approx. 5 mg. The heating rate during the run was 20 °C/min.

3. Results and Discussion

3.1. Chemical Strucutre

3.1.1. Fourier-Transform Infrared Spectroscopy

FTIR is a useful method for determining the chemical composition of materials. The IR spectrum is used for identification. In this study, the qualitative and quantitative composition of the product was not determined, but mainly the spectrum obtained was compared with that of a standard sample. In the first step of the research, prepolymers PRE_PRIPL_6, PRE_PRIPL_8, PRE_PO3G_6, and PRE_PO3G_8 were synthesized. Spectra of obtained ether and ester-urethane prepolymers, and also monomers which were used for their preparation are presented in Figures 1 and 2.

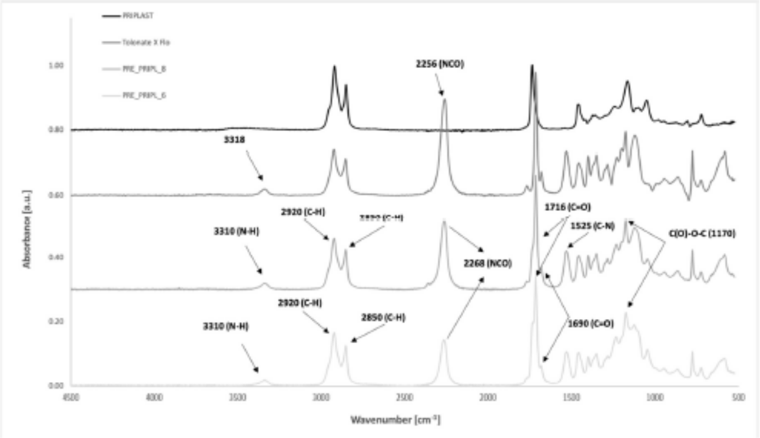


Figure 1. FTIR spectra of ester-urethane prepolymers and monomers.

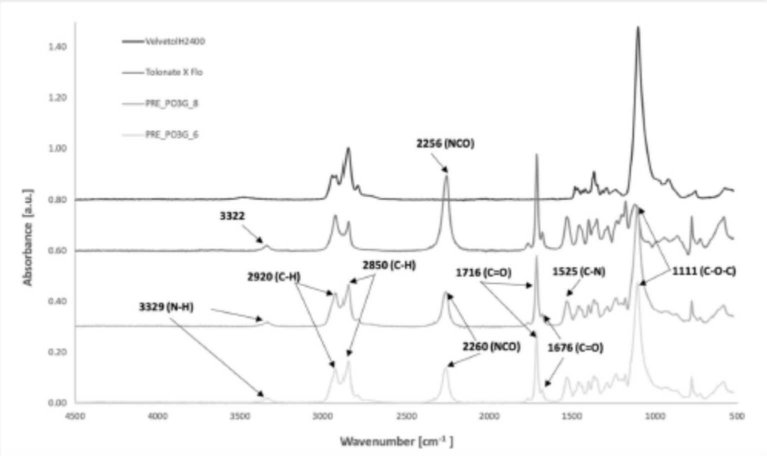


Figure 2. FTIR spectra of ether-urethane prepolymers and monomers.

Figure 1 shows FTIR spectra for polyester polyol, partially bio-based isocyanate and prepolymers with ca. 6% and 8% of unreacted NCO groups. For each sample, characteristic functional groups were identified. Spectrum analysis of monomers and prepolymers allows to confirm the appearance of new bands related to the course of reaction between polyols and isocyanates. The FTIR spectra for all prepolymers (PRE_PO3G_6, PRE_PO3G_8, PRE_PRIPL_6 and PRE_PRIPL_8) are similar considering the presence of urethane and isocyanate groups, but differ in the intensity and location of the individual absorption peaks of the polyols. The formation of a urethane group characteristic for urethanes prepolymers and polyurethanes is confirmed by the band corresponding to stretching vibrations of -NH group of urethane group at wavenumber 3310 cm^{-1}. Furthermore, bands were observed at a wavenumber between 2300–2200 cm^{-1}, originating from stretching vibrations of the isocyanate group, confirmed by the Tolonate X Flo 100 spectrum [22]. It means that the excess of isocyanates was used and unreacted isocyanate groups, which are essential for the reaction with the chain extender, were still present at the terminal end of the prepolymer chain. Moreover, changes related to the band intensity coming from stretching vibrations of NCO groups were observed. An increase in the content of free isocyanate groups (%) in the prepolymer resulted in an increase in the area of this band, which confirms an increase in the number of these groups in the structure of the synthesized urethane prepolymer. Moreover, in the range of 1525–1530 cm^{-1} we observed a vibration stretching of the C-N bond and bending vibrations of -NH bonds in the urethane moiety [1]. Nevertheless, the greatest changes were observed in the band corresponding to valence vibrations of the NCO group. These vibrations, depending on the synthesis duration, differ in intensity and the area under the peak. Characteristic vibrations of the unbound C=O group of the urethane bond (1716 cm^{-1}) and a band at the value of 1690 cm^{-1} were assigned [23]. At the region of carbonyl group vibration, derived from urethane linkage, also occurs the vibration of ester-based carbonyl characteristic for polyester polyol moiety. The band with a wavenumber of 1250 cm^{-1} indicates the presence of ester bonds present in Priplast. We also observe stretching vibrations of C-H bonds in the range of 2800–3000 cm^{-1} [23]. Asymmetric bending vibrations for the C-H bonds in CH_2 group occur at a wavenumber of 1460 cm^{-1}, while symmetrical vibrations are observed at the value of 1378 cm^{-1} [1]. It is observed that absorption bands of ester-urethane prepolymer with ca. 8% content of unreacted NCO groups (PRE_PRIPL_8) were analogous to those of PRE_PRIPL_6 prepolymer. The observed differences result from the change in the concentration of the unbound isocyanate groups and hence the differences in the intensity and area of the absorption bands of the isocyanate group. Vibrations of the unbound C=O group (1714 cm^{-1}) and the bands at the value of 1690 cm^{-1} of PRE_PRIPL_8 sample are also characterized by higher intensity than in PRE_PRIPL_6 sample [24].

In Figure 2 spectra of ether-urethane prepolymers, polyether polyol and partially bio-based isocyanate were presented. For prepolymers PRE_PO3G_6 and PRE_PO3G_8, characteristic vibrations of the N-H bond, C-N bond, and C=O bond of the urethane group were also observed. The difference between ester and ether-urethane prepolymers is because the stretching vibrations of the carbonyl group was assigned as a double band at the value of 1734-1690 cm^{-1} [25]. The valence vibration of the NCO group was assigned at 2270 cm^{-1}. Moreover, stretching vibrations were observed for the C-O-C group at a wavenumber of 1111 cm^{-1} for the polyol ether group present in PO3G [26]. The wavenumbers of C-H bond in CH_2 group for stretching and bending vibration occurred at the range of 2800–3000 cm^{-1} and 1378–1460 cm^{-1}, respectively.

3.1.2. Proton Nuclear Magnetic Resonance

Figures 3 and 4 present the spectra of Tolonate X FLO 100 and of the obtained ester-urethane and ether-urethane prepolymers.

The exact chemical formula of Tolonate X FLO diisocyanate was not disclosed by the manufacturer, however its structure was analyzed by a group of researchers from the University of Montpellier [21]. The NMR spectrum in Figure 3 shows several intense signals at 3.5 ppm, 2.5 ppm, 1.2 ppm. The signal at 3.5 ppm corresponds to the poly(ethylene glycol) chain. Protons of -CH_2 groups, which are located inside the aliphatic chain of bio-diisocyanate, and protons of -CH_3 group were observed in the range of 0.8–1.7 ppm. Meanwhile, the signal at 2.5 ppm was assigned to the protons of the solvent used $(CD_3)_2SO$ (dDMSO). Based on the publication of Morales-Cerrada et al. it was concluded that the bio-based part of Tolonate X Flo is the palmitic acid moiety, while the poly(ethylene glycol) and chains containing isocyanate groups are derived from petroleum-based substances (ethylene glycol and hexamethylene diisocyanate) [21].

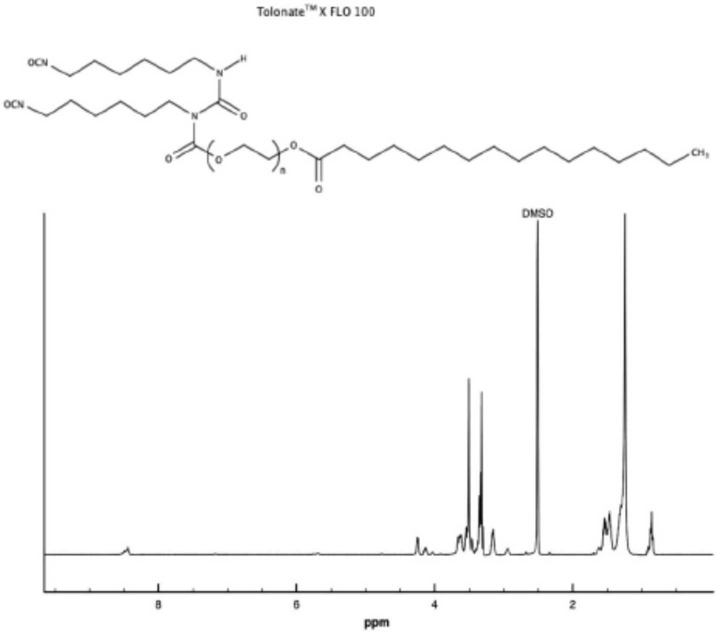


Figure 3. ^{1}H NMR spectra of Tolonate X FLO 100 sample.

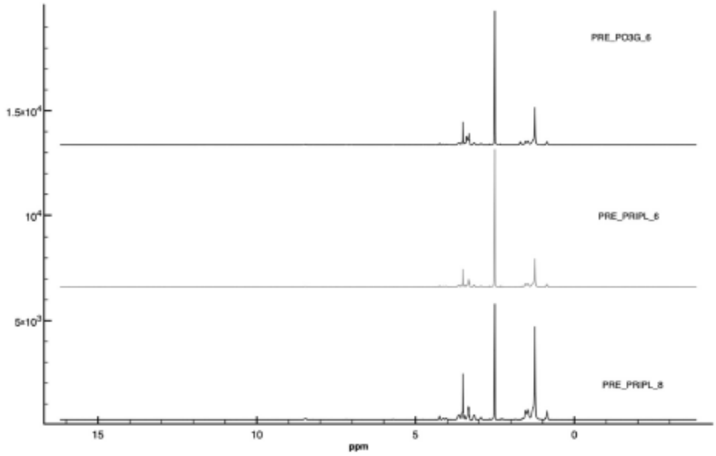


Figure 4. ^{1}H NMR spectra of PRE_PRIPL_6, PRE_PRIPL_8 and PRE_PO3G_6 prepolymers.

Figure 4 presents a spectrum comparison for polyester-urethane and polyether-urethane prepolymers. Based on the analysis of ^1H NMR spectra, it was found that a reaction occurred between the -NCO group of the diisocyanate and the -OH group of the polyol used because a signal appeared in the range of the chemical shift of 8.52–8.42 ppm, characteristic of the protons in the -NH group of the urethane group [27]. The low intensity of this signal may be due to the unusual structure of the isocyanate, which does not contain aromatic rings that are present in typical isocyanates used for polyurethane synthesis. In the range of 3.69–3.58 ppm, numerous signals were observed associated with protons of the -CH_2 groups which are linked to the oxygen atom of the ester group. In contrast, protons linked to the oxygen atom of the urethane group and the nitrogen atom of the urethane group were located at 3.57–3.1 ppm. At a shift value of 2.98–2.8, protons were observed in the immediate vicinity of the isocyanate group. Meanwhile, protons of -CH_2 groups, which are located inside the aliphatic chain of bio-diisocyanate, bio-polyol and protons of -CH_3 group were observed at a shift range of 2.98–0.8 ppm.

3.2. Processing Properties

3.2.1. Rheological Measurement

Determining processing properties of prepolymers and polymers is necessary for the proper conduct of technological processes. The properties are assessed by adjusting the flows to the conditions in the processing tools [12]. Rheological measurements are used in many industries, including process engineering, bioengineering, or soil mechanics [28]. The combination of rheological studies and the structure and thermal properties of the prepolymer used allows for the best possible adjustment of the processing conditions.

The main parameter determined in rheological tests is viscosity. Viscosity describes resistance that occurs in a material as some layers move relative to others.

The rheological analysis provided information on the dependence of viscosity in the function of shear rate (Figure 5), and on the dependence of shear stress in the function of shear rate (Figure 6). The measurements were carried out at 60 °C, 70 °C, and 80 °C, and the share rate was at the range from 0 to 300 s^{-1}.

3.2.2. Viscosity Curves of Prepolymers

Depending on the polyol which was used, the studied prepolymers show significant differences in viscosity curves and flow curves. Based on Figure 5, it was found that ether-urethane prepolymers have lower viscosities than ester-urethane prepolymers. In practice, ether-urethane prepolymer is a better processing material. Lower viscosity of the raw material is more advantageous in the preparation of polyurethane materials as it facilitates introduction of the filler and as a result it is possible to ensure a higher homogenization of the system. The course of the viscosity curve shows that both prepolymers belong to shear-thickening liquids and dilatation fluids, which means that their viscosity increases with the increasing shear rate [29]. For prepolymers with a higher content of free isocyanate groups, greater differences in viscosity are evident: at T = 60 °C for ca. 8% of unreacted NCO group the viscosity is about 0.8, and for NCO = 6% it is 0.7.

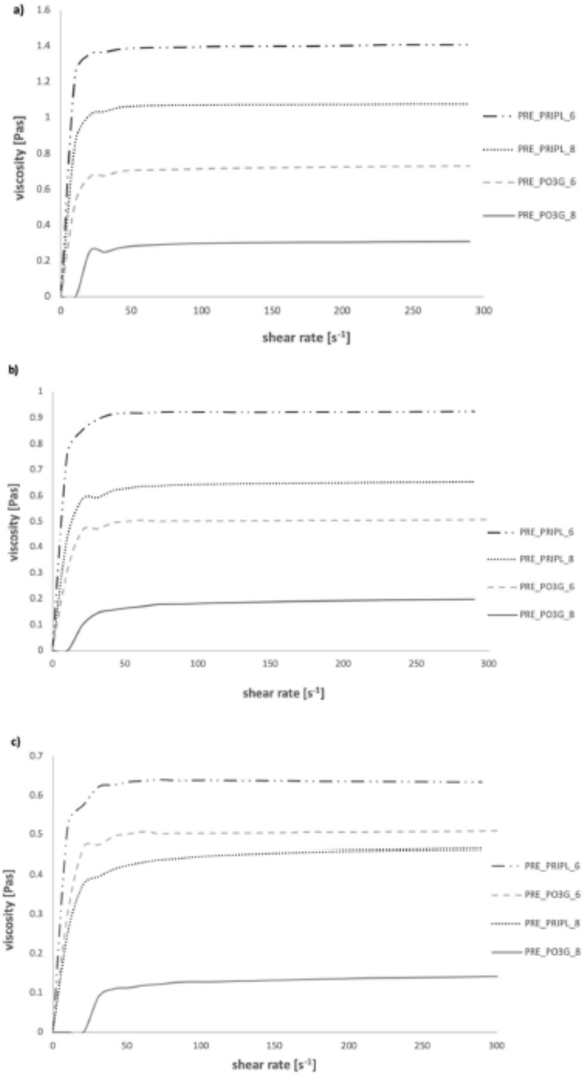


Figure 5. Viscosity curves of the synthesized bio–based polyols at (**a**) 60 °C, (**b**) 70 °C, (**c**) 80 °C.

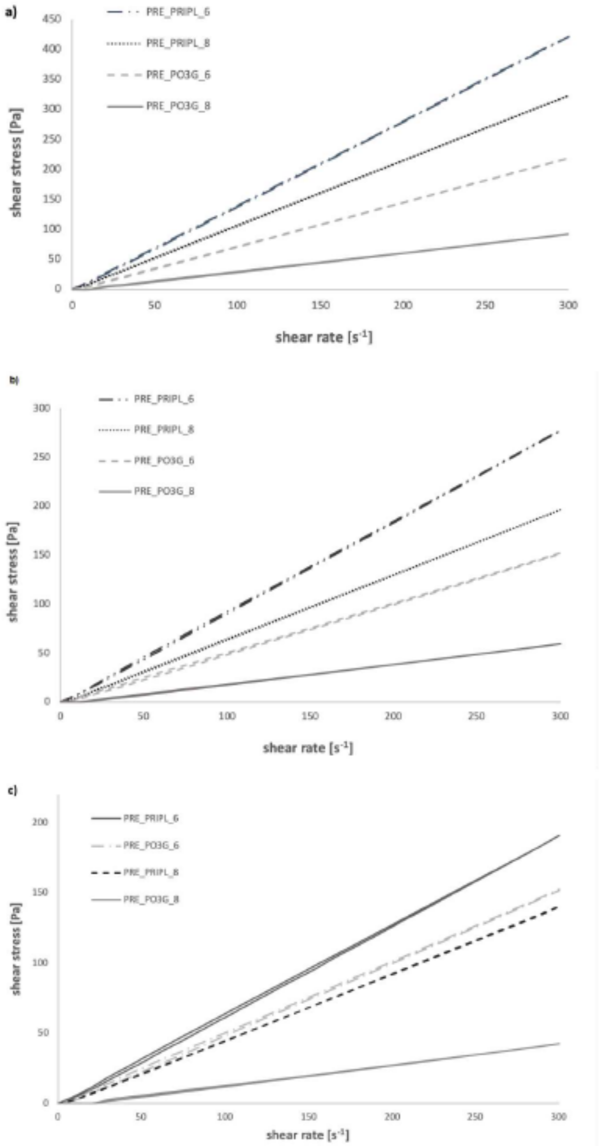


Figure 6. Flow curves of the synthesized bio−based polyols at (**a**) 60 °C, (**b**) 70 °C, (**c**) 80 °C.

3.2.3. Flow Curves of Prepolymers

In Figure 6, it is observed that the ascending curve for prepolymers with ca. 8% of unreacted NCO groups is above the descending curve, which means that the liquids are thixotropic. Moreover, at a temperature of 60 °C, it was observed that the curves coincide in both directions, which means that the fluid is rheologically stable. On the other hand, at T = 70 °C and T = 80 °C, slight hysteresis loops related to the destruction of the structure were recorded (Figure 6). In case of flow curves for prepolymers with ca. 6% content of unbound NCO groups, no hysteresis loops were noticed, which means that with shear forces acting, the structure was not destroyed. For PRE_PO3G_6 and PRE_PRIPL_6 prepolymers at T = 60 °C, the descending curve was observed above the ascending curve, which means that the liquid is anti-thixotropic. As for the viscosity curves and flow curves recorded at temperatures: 70 and 80 °C, their course is similar to that of the prepolymers tested at T = 60 °C. An increase in temperature reduces the differences in viscosity of the tested prepolymers. The differences in the maximum viscosity are as follows: at T = 60 °C–0.8 Pa·s, at T = 70 °C–0.4 Pa·s, and at T = 80 °C–0.1 Pa·s. No hysteresis loops were observed for the flow curves at T = 70 °C. A difference in the course of the flow curve was observed at T = 80 °C. The ascending curve was above the descending curve, which means that the liquid is thixotropic. In addition, a slight hysteresis loop appears, which indicates that the structure is damaged by shear forces.

For all the temperatures, it was found that the dynamic viscosity coefficient increases with the increase in the shear rate, which allowed us to classify the fluids as shear thickened, and dilatation.

Based on the data in Figure 5, we could conclude that ester-urethane prepolymer with ca. 6% of unbound NCO groups was characterized by the highest viscosity. On the other hand, the lowest viscosities were displayed by ether-urethane prepolymer with 8% content of free NCO group. It was also observed that prepolymers with ca. 6% free NCO group were characterized by higher viscosity than prepolymers with higher content of NCO groups. These results show a significant influence of the content of free isocyanate groups, and of the substrate used on the viscosity of the systems. Systems with lower viscosities are more advantageous to use, especially in industry. We observed a characteristic decrease in viscosity with increasing temperature for all the prepolymers studied.

Table 2 shows a comparison of the best-fitted models with constants for the obtained prepolymers. The R parameter value indicates the degree of adjustment to a given model. All the models were determined using Rheo3000 software. Most of the samples were characterized with the Hershel-Bulkley rheological model, only two of the samples were described by another model. The sample of PRE_PRIPL_6 at 80 °C was described by the Newton model, and the sample of PRE_PRIPL_8 at 60 °C by the Ostwald model. The formulas for each model are presented below (Table 2).

3.3. *Thermal Stability*

Thermogravimetry

Thermogravimetric analysis is used in the thermal analysis of materials. Characterization of samples is performed by measuring changes in sample mass as a function of temperature.

The thermal properties of prepolymers and polyurethanes greatly depend on the substrates used in their synthesis. Due to the emission of gaseous products, their thermal degradation is a very complex process. Thermogravimetric curves provide information on the segmental structure of polyurethane materials and allow the determination of the percentage variation of the sample mass as a function of temperature.

Table 2. Rheological model of the obtained prepolymers.

Sample Code	Equation	k_1	k_2	k_3	R
PRE_PO3G_6 (60 °C)	$y = 0.65x^{1.02}$	0	0.65	1.02	0.9999
PRE_PO3G_6 (70 °C)	$y = 0.47x^{1.01}$	0	0.47	1.01	0.9999
PRE_PO3G_6 (80 °C)	$y = 0.38x^{0.99}$	0	0.38	0.99	0.9998
PRE_PO3G_8 (60 °C)	$y = 0.25x^{1.04}$	0	0.25	1.04	0.9998
PRE_PO3G_8 (70 °C)	$y = 0.12x^{1.09}$	0	0.12	1.09	0.9996
PRE_PO3G_8 (80 °C)	$y = 0.08x^{1.10}$	0	0.08	1.10	0.9998
PRE_PRIPL_6 (60 °C)	$y = 1.34x^{1.01}$	0	1.34	1.01	0.9999
PRE_PRIPL_6 (70 °C)	$y = 0.90x^{1.01}$	0	0.90	1.01	0.9999
* PRE_PRIPL_6 (80 °C)	$y = 0.65x$	a	0.65	-	0.9999
** PRE_PRIPL_8 (60 °C)	$y = x^{1.01}$	0	1	1.01	0.9999
PRE_PRIPL_8 (70 °C)	$y = 0.59x^{1.02}$	0	0.59	1.02	0.9999
PRE_PRIPL_8 (80 °C)	$y = 0.37x^{1.04}$	0	0.37	1.04	0.9998

* The best rheological model–Newton; ** Ostwald's best model; a—not applicable.

Thermal decomposition of urethane prepolymers and polyurethane materials occurs in several stages. Thermogravimetric curves of the synthesized urethane prepolymers are shown in Figures 7–10. The DTG and TG curves show that the decomposition of prepolymers displays a three-step-mass loss tendency. Thermogravimetric analysis of monomers clearly indicated which step in the decomposition of the prepolymers originated from each component.

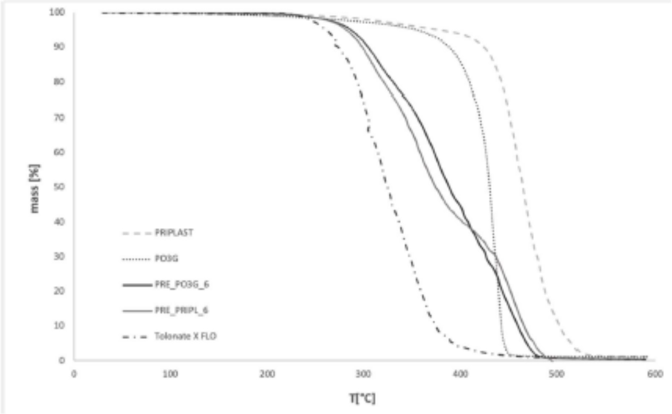


Figure 7. Dependence of TG in function of temperature for monomers and the obtained bio-based prepolymers with NCO ca. 6%.

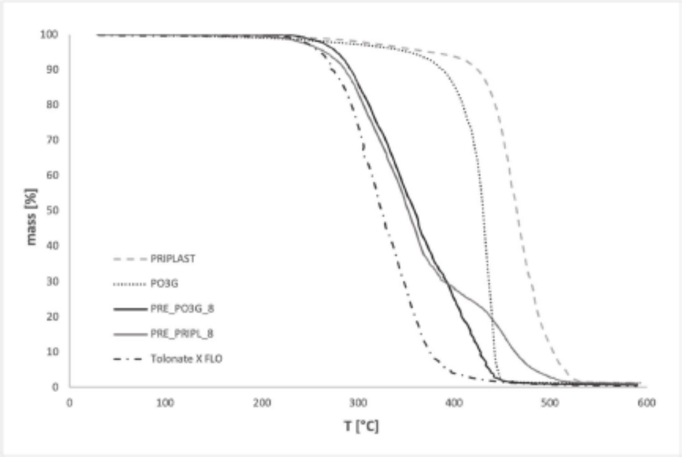


Figure 8. Dependence of TG in function of temperature for monomers and the obtained bio-based prepolymers with NCO ca. 8%.

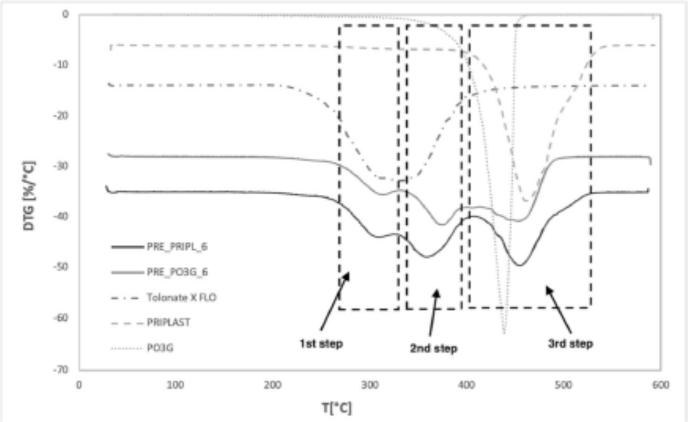


Figure 9. Dependence of DTG in the function of temperature for monomers and the obtained bio−based prepolymers with NCO ca. 6%.

Usually, during the decomposition of polyurethane materials, the first step is related to the decomposition of hard segments which consist of diisocyanate and low molecular weight chain extender [24,25]. In the case of urethane prepolymers, the first stage is related to the dissociation of unreacted diisocyanate. This stage is similar for all four urethane prepolymers, is associated with the degradation of the unreacted isocyanate, and occurs in the temperature range 233–321. The second stage occurs in the temperature range 350–380 and is associated with the dissociation of urethane group. The third stage of degradation is related to the decomposition of polyol [24]. As seen in Figures 7 and 8, degradation of the ester-urethane prepolymer occurs at a higher temperature than that for ether-urethane prepolymer, which is related to a greater proportion of hard segments that degrade first.

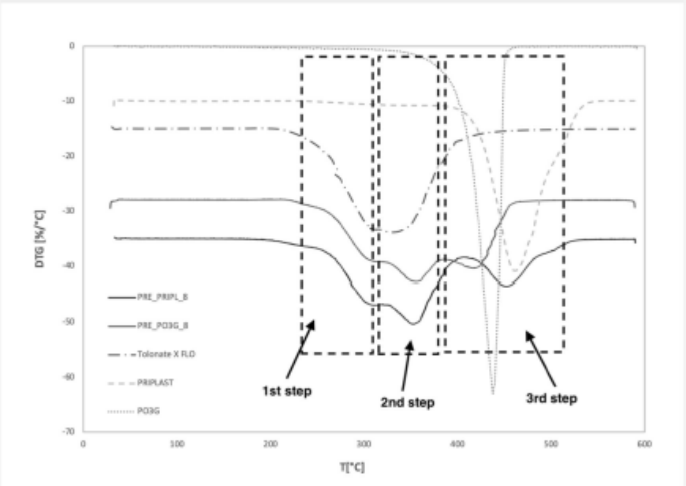


Figure 10. Dependence of DTG in the function of temperature for monomers and the obtained bio−based prepolymers with NCO ca. 8%.

Analyzing the thermal stability of used monomers, Table 3 shows a dependence in which the loss of 5% by weight of ester polyol occurs at a higher temperature (376.7 °C) than that for ether polyol (353.9 °C). This is due to the branched structure of ester polyol and its higher molecular weight. The work of J. Amado also confirmed higher thermal stability of polyester polyol than of polyether polyol. This is due to a general relationship in which an ether bond degrades at a lower temperature than the ester bond [30]. Table 3 presents a summary of temperatures at which the weight loss for selected monomers and bio-based urethane prepolymers was 5, 10, 50 and 90%, respectively. The last column of Table 3 contains residue amounts after combustion at 550 °C.

Table 3. Thermal decomposition characteristics of the obtained bio-based materials.

Sample Code	T_5 [°C]	T_{10} [°C]	T_{50} [°C]	T_{90} [°C]	$m_{T550\,[°C]}$ [%]
PO3G	353.9	387.9	429.9	441.9	1.1
PRIPL	376.7	424.1	464.8	502.7	1.3
FLO	261.5	274.2	324.7	374.5	0.45
PRE_PRIPL_6	280.0	297.8	372.3	475.1	1.1
PRE_PO3G_6	286.4	303.9	388.3	459.4	0.4
PRE_PRIPL_8	266.9	286.2	352.4	463.1	1.24
PRE_PO3G_8	277.9	292.2	358.4	426.9	0.8

T_5 is the temperature of 5% mass loss, T_{10} is the temperature of 10% mass loss, T_{50} is the temperature of 50% mass loss and T_{90} is the temperature of 90% mass loss.

4. Conclusions

To sum up, we studied four novel bio-based isocyanate-terminated polyurethane prepolymers obtained with the use of two types of polyols: polyether and polyester, both of renewable origin, in the reaction with excess bio-based isocyanate (with 32% content of green carbon). Prepolymers with the content of ca. 6% and 8% unreacted isocyanate group were obtained. The chemical formula of the obtained prepolymers was confirmed by FTIR and NMR analysis. The two types of prepolymers are different in regard to their rheological properties, irrespective of NCO content. Polyester-based prepolymers were characterized by over 200% higher viscosity at the temperature of 60 °C than polyether-based prepolymers. In general, viscosity depends on temperature, and at a higher temperature lower differences in viscosity between both types of prepolymers were observed.

In general, it was demonstrated that both prepolymers degraded in three steps, similar to polyurethane materials. Their thermal stability is closely related to the type of bio-based polyols which were used for the pre-polymerization process. The beginning of thermal degradation expressed as $T_{5\%}$ is about 10 °C higher for urethane prepolymers based on PO3G polyol.

A proper understanding of the influence of the structure on rheological properties of substances allows for designing an optimal model of the materials manufacturing process. Obtained bio-based prepolymers have a high content of green carbon and because of their good rheological characteristics and thermal stability, they can be processed, for example, by using an industrial grades technique such as RIM (reactive injection molding technique). It is also possible to obtain foamed or cast materials with the use of prepared urethane prepolymers. Polyurethanes obtained with the use of bio-based urethane prepolymers can exhibit many important functional properties such as high elasticity, good abrasion resistance and good vibration damping properties. The properties of these materials can be freely modified by appropriate selection of components, synthesis conditions, and ratios of individual substrates.

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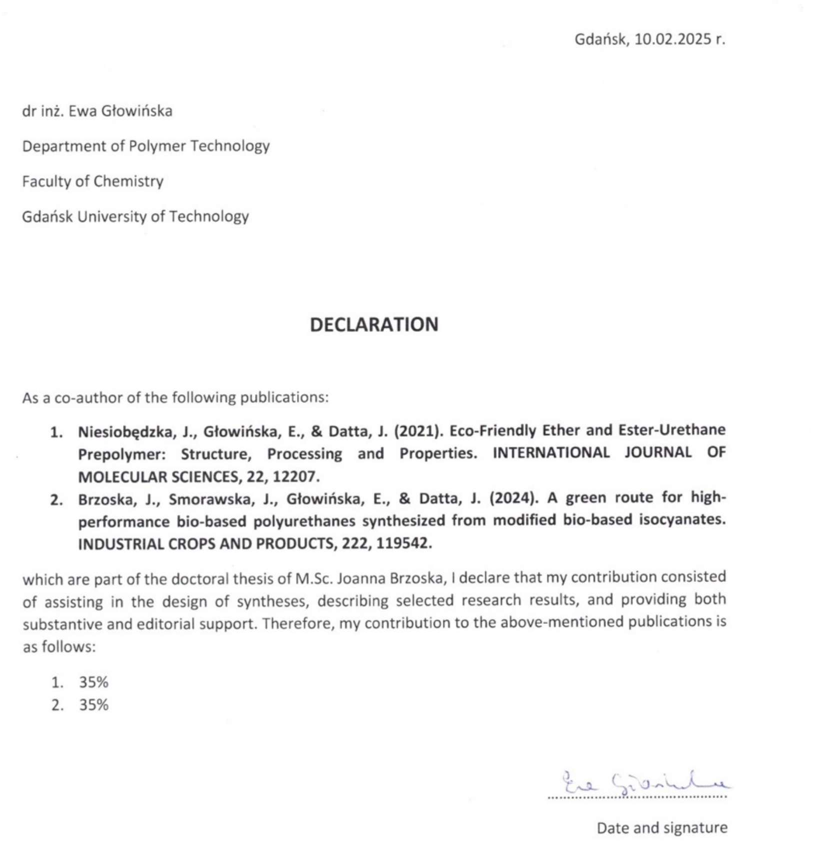
Co-authors’ statements of contribution



Gdańsk, 10.02.2025 r.

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DECLARATION

As a co-author of the following publications:

1. **Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.**
2. **Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.**

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of assisting in the design of syntheses, describing selected research results, and providing both substantive and editorial support. Therefore, my contribution to the above-mentioned publications is as follows:

1. 35%
2. 35%

....

Date and signature

Gdańsk, 07.03.2025 r.

Prof. dr hab. inż. Janusz Datta

Department of Polymer Technology

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Gdańsk University of Technology

DECLARATION

As a co-author of the following publications:

1. Niesiobędzka, J., & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.

2. Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.

3. Brzoska, J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.

4. Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of providing consultation during the execution of the experimental work, evaluating the literature review, and proofreading the papers. Therefore, my contribution to the above-mentioned publications is as follows:

1. 30%

2. 15%

3. 15%

4. 10%

……………………………………

Date and signature

3.3. Brzoska, J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.		
Article title	The influence of bio-based monomers on the structure and thermal properties of polyurethanes.	
Author's contribution	I was responsible for preparing a significant portion of the manuscript and conducting the synthesis of the materials described in the publication. Additionally, I carried out the analysis and interpretation of FTIR, DSC, TGA, and TG-FTIR results.	
Percentage contribution	**Joanna Brzoska**	**54%**
	Janusz Datta	15%
	Rafał Konefał	8%
	Vaclav Pokorny	8%
	Hynek Benes	15%

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The influence of bio-based monomers on the structure and thermal properties of polyurethanes

Joanna Brzoska[1], **Janusz Datta**[1]✉, **Rafał Konefał**[2], **Václav Pokorný**[2] & **Hynek Beneš**[2]

Most polyurethanes (PU) are currently produced through the polyaddition reaction of polyisocyanates with polyols and chain extenders, using components of petrochemical origin. From an environmental and geopolitical point of view, and with regard to the problems of oil supply and processing, the replacement of petrochemical PU raw materials with renewable resources is highly desirable. It is also one of the principles of sustainable development and an important challenge for chemical companies and market competitiveness. Current research studies focus mainly on the use of bio-based polyols for PUs, while other PU components, in particular polyisocyanates, remain of petrochemical origin. In this work, a series of PUs have been synthesized by polyaddition reactions of different types of renewable polyols and bio-based polyisocyanates. The effects of the bio-derived components on the structure, thermal stability and phase transformations of the PU were studied using FTIR and NMR spectroscopy, SWAXS, TGA, DSC, DMTA and TGA-FTIR. A full conversion of the bio-based monomers was achieved in all cases, indicating good compatibility and reactivity of all bio-based components. It was observed that bio-based PU exhibited a lower degree of phase separation and slightly lower thermal stability compared to PUs from petrochemical monomers.

Keywords Sustainable development, Climate change, Natural resource, Biomass, Polyurethane

Commercial, polyurethanes (PU)s are obtained by the polyaddition reaction of di- or polyisocyanates with polyols and chain extenders[1–3]. Polyols and isocyanates are the main components of the formulation, which significantly determine the properties of the PU materials[4,5]. The amount of isocyanate in the formulation is generally around 30–40 parts by weight. The isocyanate-derived parts of PU structure can form hard segments (HS), which are responsible for the hardness, mechanical strength, and thermal stability of PU materials[6–8]. Unfortunately, the commercial-available isocyanates are of petrochemical origin, obtained by the reaction of amines with toxic phosgene. Isocyanate synthesis is highly unfavorable, dangerous to human health and not environmentally friendly[7,9,10]. Therefore, research has been carried out to find alternative and more environmentally friendly solutions to produce isocyanates using a safer synthesis route and non-petrochemical raw materials[11].

Up to now, only a few bio-based polyisocyanates have been described in the literature[12–14]. Commercially available polyisocyanates are mainly derived from plants (fatty acids). Currently, there are three main types of bio-based isocyanates on the market: 1,5-penthamethylene diisocyanate (PDI) and its oligomers; L-lysine ethyl ester diisocyanate (LDI)[15]; and diisocyanate derived from 1,6-hexamethylene diisocyanate (HDI) and palm oil[16]. Covestro produces bio-derived PDI from plant sugars using a synthesis process that significantly reduces energy consumption. The PDI has a green carbon content of over 71% and although this bio-based monomer is not commercially available, it is further used to synthesize an aliphatic PDI trimer. This trimer is available on the market under the trade name DESMODUR® eco N 7300[17] and is dedicated to the synthesis of PU coating systems that are resistant to light, weather, and scratches[17].

Aliphatic polyisocyanurates based on bio-based 1,5-pentamethylene diisocyanate is produced by Mitsui Chemicals under the trade name STABIO™ PDI. The offered monomer is available in two variants with low and high viscosity. The company recommends to use it for the synthesis of PU-urea materials[18].

Another bio-based diisocyanate producer is Vencorex Chemicals, which offers an aliphatic bio-monomer under the trade name Tolonate™ X FLO 100. It is obtained from vegetable oil derivatives with a green carbon

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content of up to 32%. This monomer is used for the synthesis of elastomers and PU coatings[16]. As the exact chemical formula of this diisocyanate was not disclosed by the manufacturer, the authors of the publication "Fully Bio-Based Thermosetting Polyurethanes from Bio-Based Polyols and Isocyanates" proposed its structure based on electrospray ionisation mass spectrometry (ESI-MS negative)[19]. Based on this, Tolonate™ X FLO 100 contains a long-chain side group (labelled RO-) derived from vegetable oils. This complicates the synthesis of PUs due to the presence of additional functional groups and double bonds in the RO- labeled bio-diisocyanate fragment, resulting in additional cross-linking of the material.

The raw materials market for the synthesis of PUs also includes L-lysine ethyl ester bio-diisocyanate (LDI)[20]. It is produced from the amino acid L-lysine extracted from plant biomass. The LDI-based PUs exhibit low toxicity and biodegradability[21].

Furthermore, companies like General Mills Inc[22,23]. and BASF Europe[24] have developed isocyanates derived from fatty acid dimers. These innovative compounds have found applications in multiple industries, particularly in the production of ultraviolet-curable coatings, where they offer enhanced performance and sustainability.

It is well known that some applications require PUs to have special properties, including resistance to very high temperatures. For example, high-temperature resistant adhesives are required in advanced aircraft, rockets, and ground vehicles[25]. Therefore, an important parameter determined in the analysis of PU materials is their thermal stability, which describes the thermal durability of PU[26]. Polymers with higher thermal stability have higher melting, softening, and thermal decomposition temperatures, lower weight loss during heating at high temperatures, without losing their basic properties[27]. Various tests are carried out to evaluate these properties, including thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC). This paper focuses on a detailed analysis of the structure and thermal stability of the obtained bio-based PUs as promising alternatives to the current petrochemical PUs.

In this work, renewable monomers were used to synthesize bio-based PU by polyaddition reaction. The reference PU materials were prepared from the petrochemical polyols and hexamethylene diisocyanate, using 1,3-propanediol as a chain extender. Meanwhile, the preparation of polyurethanes based on bio-based monomers with desired thermal properties remains an open challenge. Here, we describe the synthesis and characterization of novel polyurethanes based on bio-based PO3G (polyether polyol), semi-crystalline, bio-based polyester polyol (Priplast 3294), and partially bio-based isocyanate Tolonate X FLO 100 with bio-based chain extender 1,3-propanediol. Fourier Transform Infrared (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) and Small and wide-angle X-ray scattering (SWAXS) were used to characterize all samples. The thermal properties of PUs were studied by TGA, DSC, DMTA and combination of FTIR spectroscopy and thermogravimetric analysis (TG-FTIR).

Experimental

Materials

For reference samples, two types of polyols were used: polyether polyol - poly(tetramethylene glycol) (PTMG) supplied by Overlack (Ozorków, Poland) and polyester polyol - Polios 55/20 purchased from Purinova (Bydgoszcz Poland) both with a molecular weight of 2000 g/mol. Hexamethylene diisocyanate (HDI), 1,3-propanediol (PDO) and catalyst dibutyltin dilaurate were purchased from Sigma Aldrich (Saint Louis, USA) and used as received. The reaction inhibitor was orthophosphoric acid supplied by POCH Gliwice (Gliwice, Poland).

For the synthesis based on renewable raw materials we used aliphatic isocyanate Tolonate X FLO 100 purchased from Vencorex (Saint-Priest, France) and two types of polyols: polyester polyol - PRIPLAST 3294™ purchased from Croda (Snaith, UK) and polyether polyol - Velvetol H2000 supplied by Allessa GmbH (Frankfurt, Germany) both with a molecular weight of 2000 g/mol. The chain extender Zemea (1,3-propanediol) was purchased from DuPont Tate & Lyle Bio Product (Naucalpan de Juárez, USA). The same catalyst and inhibitor were used as for the reference samples. The chemicals were used without further purification unless stated otherwise.

Synthesis of PU elastomers

The PUs were obtained using a two-step prepolymer method. The first step was to synthesize the prepolymer by reacting the polyol with an excess of diisocyanate at 85 °C for 2 h under vacuum. During the reaction, the percentage of NCO groups were determined by titration according to ISO 14896:2010 (isocyanate is reacted with an excess of n-dibutyl amine to form substituted ureas. The excess dibutyl amine is then back-titrated with aqueous hydrochloric acid. The solvent used is acetone). A chain extender and catalyst (0.1% DBTL) were then added to the prepolymer, and the mixture was stirred for 60 s. and degassed under vacuum for 60 s. The molar ratios of [NCO]/[OH] groups was 1.05. Finally, the materials were cured in a laboratory oven at 80-100 °C for 24 h. Figure 1 shows the overall method for the synthesis of ethers and ester-urethanes from bio-based monomers. Table 1 presents the formulation of the synthesized samples, the content of unreacted isocyanate groups in prepolymers (NCO content) and the content of HS. The content of bio-monomers (bio-content) was calculated using Eq. (1) and is given in Table 1.

$$bio - content = \frac{M_{BIO}}{M_{TOTAL}} \times 100\% \quad (1)$$

M_{BIO} - the molar mass of the used bio-monomers. M_{TOTAL} – the molar mass of all substrates used.

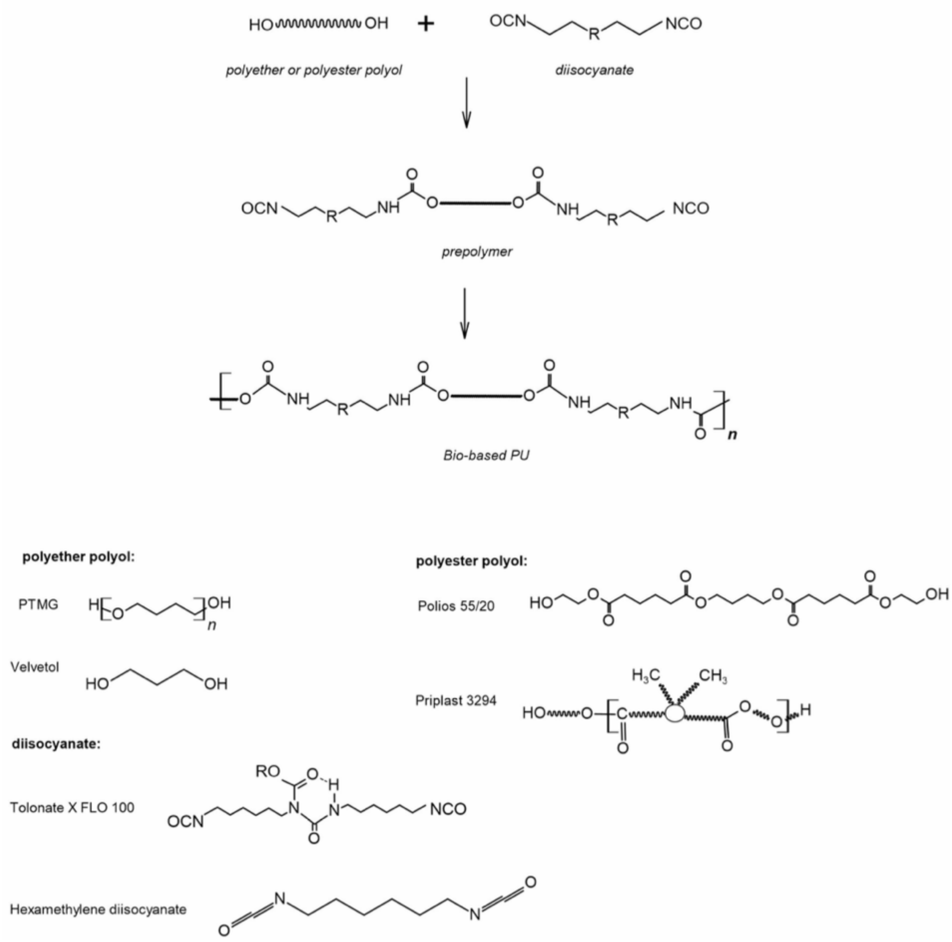

Fig. 1. Reaction scheme for ether- and ester-urethane prepolymers formation.

Sample code	Polyol	Isocyanate	Glycol	NCO content [%]	HS content [%]	Bio-based content in PU [%]
HPoP	Polios 55/20	HDI	PDO	7.8	27.5	0
HPTP	PTMG	HDI	PDO	7.7	27.4	0
TPobP	Polios 55/20	Tolonate X FLO 100	bio-PDO (Zemea)	7.5	41	23.8
TPTbP	PTMG	Tolonate X FLO 100	bio-PDO (Zemea)	7.7	41	23.8
TVbP	Velvetol H2000	Tolonate X FLO 100	bio-PDO (Zemea)	7.7	41	52
TPribP	Priplast 3294	Tolonate X FLO 100	bio-PDO (Zemea)	7.8	41	52

Table 1. Sample summary.

Methods of characterization

Fourier transform infrared spectroscopy

The chemical structure of the bio-based PU was analyzed by Fourier Transform Infrared Spectroscopy using a Spectrum 100T FT-IR spectrometer with universal ATR accessory (PerkinElmer, USA). Each spectrum was recorded at room temperature for wavenumber range of 500 to 4500 cm^{-1} with a resolution of 4 cm^{-1}.

The degree of the carbonyl groups participating in hydrogen bonding can be described by the carbonyl. hydrogen bonding index, R, as given in Eq. (2).

$$R = \frac{A_{bonded}}{A_{free}} \tag{2}$$

where A is the intensity of the characteristic absorbance ($A_{H-bonded}$ – absorption intensity of hydrogen-bonded carbonyl; A_{H-free} – absorption intensity of free carbonyl). The degree of phase separation (DPS) and the degree of phase mixing (DPM) can be obtained by using Eqs. (3) and (4), respectively.

$$DPS = \frac{R}{R+1} \tag{3}$$

$$DPM = 1 - DPS \tag{4}$$

Nuclear magnetic resonance

^{1}H NMR spectra of prepared solutions (DMSO or DMF) were acquired with the Bruker Avance III spectrometer operating at 600.2 MHz. The width of 90° pulse was 18 μs, relaxation delay 10 s, acquisition time 2.73 s, 32 scans.

Small and wide-angle X-ray scattering

The internal microstructure of PU samples was investigated through Small-Angle and Wide-Angle X-ray Scattering (SAXS and WAXS) analysis. The measurements were conducted using a pinhole camera (MolMet, Rigaku, Japan, modified by SAXSLAB/Xenocs) connected to a microfocused X-ray beam generator (Rigaku MicroMax 003) operating at 50 kV and 0.6 mA (30 W). Scattering intensities were recorded using a vacuum-compatible hybrid photon-counting detector (Pilatus3 R 300 K), with a sample-to-detector distance of 1000 mm (SAXS) and 50 mm (WAXS), respectively, using an exposure time of 3 h.

Thermogravimetric analysis

TGA of the PUs were performed using a Pyris 1 TGA Thermogravimetric Analyzer (PerkinElmer, USA). Approximately 10 mg of the sample was placed in a ceramic crucible and heated from 35 to 600 °C at a heating rate of 10 °C/min under a nitrogen flow of 20 mL/min. The standard deviation of the TGA measurement was under 5%.

Differential scanning calorimetry

The thermal behaviour of the polyurethanes was evaluated by differential scanning calorimetry (DSC) using a TG 209F1 Libra (NETZSCH, Germany). The samples (5–10 mg) were encapsulated in aluminium hermetic pans. The measurements were carried out in a heating-cooling-heating cycle at the temperature range of (-80) – 250 °C. The analyses were performed at a heating rate of 10 °C/min in an inert (nitrogen) atmosphere.

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG-FTIR) was carried out using a Netzsch TG 209 thermal analyser (heating rate = 10 K/min, sample mass 10–15 mg, nitrogen flow = 20 ml/min) and a Bruker Alpha FTIR spectrometer. IR spectra were recorded in the spectral range of 4000–500 cm^{-1} with a 4 cm^{-1} resolution and 8 scans.

Dynamic mechanical and thermal analysis

Dynamic-mechanical and thermal analysis (DMTA) of the prepared PU samples was measured on an ARES G2 rheometer (TA Instruments). Oscillatory shear deformation (0.02–1% strain) at a frequency of 1 Hz from – 100 °C to 150 °C at a temperature ramp rate of 3 °C/min was applied on rectangular samples (20 × 5 × 2 mm). The temperature dependence of the complex shear modulus (G^*) was observed and the main transition temperature ($T\alpha$) was determined to be the tan δ peak maximum.

Results and discussion

Fourier transform infrared spectroscopy

The chemical structure of the PUs was confirmed by FTIR-ATR and ^{1}H NMR spectroscopy. The FTIR spectra are shown in Fig. 2 and the characteristic bands are given in Table 2. The characteristic isocyanate (-N=C=O) and polyol (-OH) bands at 2260 cm^{-1} and 3600 cm^{-1}, respectively, were not observed in any of the samples[28]. Meanwhile, the bands corresponding to the urethane groups in the range of 3400–3300 cm^{-1} and the I amide band in the range of 1740–1680 cm^{-1} characteristic for the vibration of the -C=O group, confirm the full rearrangement of substrates[29,30]. At 1528–1540 cm^{-1} two vibrations were assigned to the urethane CN-H group part: a bending vibration for N–H and a stretching vibration for C–N. The band at 2937–2850 cm^{-1} can be assigned to symmetric and asymmetric CH stretching vibrations originating from the CH_2 groups present in aliphatic chains, or from the CH_3 groups. The next bands are: stretching vibrations of C–O–C in ether bonds at 1160 –1060 cm^{-1} and in ester bonds at 1250 –1150 cm^{-1}.

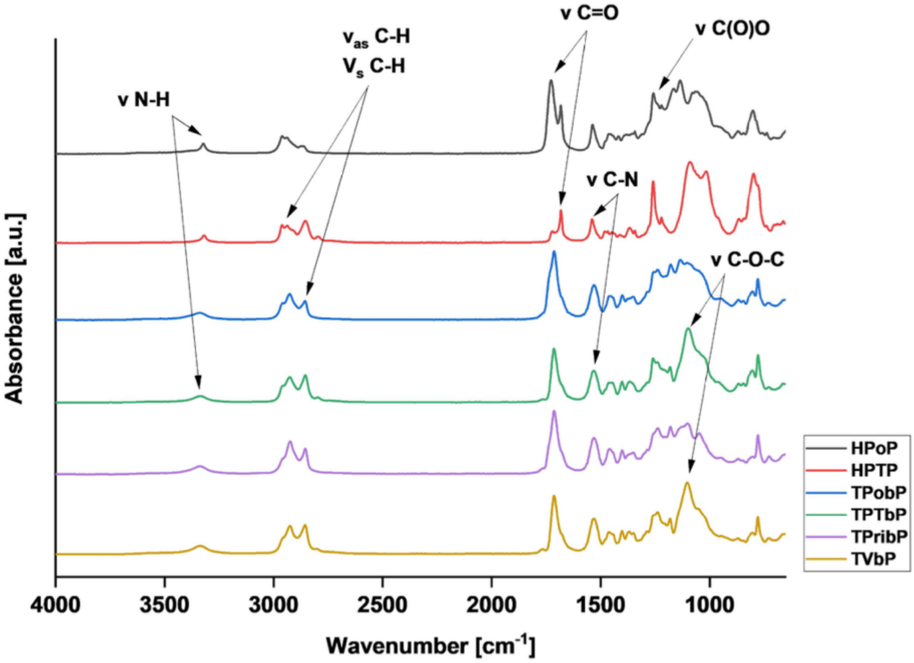

Fig. 2. FTIR spectra of PUs.

Wavenumber [cm^{-1}]	Assignments
3338–3322	-NH stretching
2933–2850	-CH_2 symmetrical and asymmetrical
1726–1681	-C=O stretching
1540–1528	-C-N stretch
1250–1150	Stretching vibrations of C(O)O in ester bonds
1160–1060	Stretching vibrations of C–O–C in ether bonds

Table 2. Characterization of selected FTIR-ATR bands of the obtained PUs.

The graphs show no significant differences in structure between the reference samples and bio-PUs, confirming the possibility of obtaining PU from bio-based monomers.

The obtained values of R, DPS and DPM for PU were given in Table 3. The DPS value describes the contribution of HS bonded among themselves by hydrogen bonds, while the DPM value describes the contribution of HS not bonded by hydrogen bonds to any other HS[31]. As has been previously reported in the literature, the DPS value in PUs increases with increasing R[32]. The HPTP sample has the highest value of R and therefore shows the highest phase separation compared to other samples. It was confirmed that the content of HS in the PU structure and the origin of the substrates used in the synthesis affect the DPS value. It was observed that as the HS content increases, DPS decreases. This is related to the fact that materials with a higher content of HS have more urethane groups, which can bond with the ester groups of polyols, increasing interactions between HS and SS and resulting in phase mixing. It was also observed that materials obtained from petrochemical monomers have higher DPS contents. This is in line with reports from other authors who also observed that the highest DPS value was recorded for HDI-based materials. This may be related to the linear structure of this isocyanate[33]. Moreover, differences were observed due to the nature of the polyol used. PUs based on polyether polyols were characterized by higher DPS values compared to PUs based on polyester polyols. For samples

Sample	**A_{bonded}^{*} (ν [cm⁻¹])**	**A_{free}^{**}(ν [cm⁻¹])**	***R***	**DPS**	**DPM**
HPTP	0.68311 (1681)	0.34143 (1695)	2.0	0.67	0.33
TPTbP	0.30617 (1692)	0.80399 (1714)	0.38	0.275	0.725
TVbP	0.29631 (1691)	0.81993 (1714)	0.361	0.265	0.735
HPoP	0.44942 (1683)	0.97873 (1726)	0.459	0.315	0.685
TPobP	0.15097 (1670)	0.91303 (1716)	0.165	0.142	0.858
TPribP	0.18518 (1673)	0.92041 (1713)	0.201	0.167	0.833

Table 3. The carbonyl hydrogen bonding index (R), the degree of the phase separation (DPS), and the degree of the phase mixing (DPM) in the obtained PUs. A: absorption intensity calculated as the area of Gaussian multipeak fitting; * A_{free}: absorption intensity of free carbonyl. ** A_{bonded}: absorption intensity of hydrogen-bonded carbonyl.

containing branched HS, i.e. based on bio-isocyanate, a decrease in DPS values was observed, probably due to the higher free volume between macromolecules, which hinders the formation of hydrogen bonds.

Nuclear magnetic resonance

^{1}H NMR spectra with a description of signals of the samples dissolved in DMSO and DMF are presented in Table 4. The type of solvent was determined by the solubility of the materials tested (due to the limited solubility of the TPTbP and TPribP samples, their spectra were prepared for prepolymers). The signals labeled a (in DMF), f (in DMSO) and k (TPribP in DMSO) in the range of 6.9–8.5 ppm are assigned to -NH in the urethane group. The peaks from 4.0 to 4.3 ppm indicate, hydrogen present in the main chain next to oxygen in the structure of this material. The range 1.2–1.7 corresponds to the protons of the methylene groups derived from the aliphatic chains of the polyol. The peaks in the range of 2.9–3.2 are related to the methylene bridge attached to the urethane nitrogen. FTIR and ^{1}H NMR analyses confirmed the reaction of the -NCO groups of the diisocyanate with the -OH groups of the polyol used, as a signal characteristic of the protons of the -NH group was observed.

X-ray scattering

All PU samples exhibit two distinct peaks in their SAXS profiles (Fig. 3), though the peak positions vary between samples. These peak positions, along with the corresponding characteristic sizes, are summarized in Table 5. The peak at lower Q-values is attributed to the microphase separation between the soft and hard segments, while the higher-Q peak corresponds to the periodic structure within the hard segment domains.

For samples containing HDI-based isocyanate, both peaks shift to higher Q-values, indicating a more compact or tightly packed structure, with smaller domain sizes. Additionally, the reduced intensity of the second peak suggests a lower hard segment (HS) content or reduced crystallinity, reflecting fewer or less well-defined hard segment domains.

The Wide-Angle X-ray Scattering (WAXS) curves (Fig. 4) reveal differences in short-range ordering between the HDI-based and Tolonate-based PU samples. These differences are likely due to variations in polymer chain arrangement and crystalline domain structure. The HDI-based samples exhibit several additional diffraction peaks, suggesting the presence of more complex or diverse structural motifs compared to the Tolonate-based PUs.

Differential scanning calorimetry

The glass transition temperature (T_g) is an important characteristic of polymeric materials because it represents the boundary between their elastic and viscoelastic behavior. Figures 5 and 6 present DSC thermograms obtained from DSC experiments during the first and second heating of PUs.

Thermal behavior of the obtained materials such as, glass transition temperature of SS (T_{gSS}) and HS (T_{gHS}), melting point of SS (T_{mSS}) and HS (T_{mHS}), and enthalpy are presented in Table 6. The T_g values mainly depended on the type of monomers. Glass transition temperatures for SS and HS and melting points for SS and HS were observed. During the first heating in the DSC, we observe melting temperatures for the reference samples, while no melting peaks are detected for the bio-based PU. This confirms our observations from the WAXS results, which show negligible crystallinity for the bio-PU, whereas the reference PU samples have a significantly higher crystalline content (17.5% for HPoP and 24.4% for HPTP). During the 2nd heating the glass transition temperature for SS is mainly observed for polyester based samples. The T_g of the soft segments ranged from − 47.4 °C to -55 °C. The lack of a distinct glass transition peak for polyether-based samples may be related to the morphological characteristics of these materials. The flexibility of the polyether-based segments could reduce the sharpness of the glass transition, making it difficult to observe a distinct T_g peak. On the other hand, melting of the soft segments is observed for the polyether-based samples and the TPobP (polyester-based) sample. This is related to the reorganization of the soft segment microdomains after the second heating cycle, as a result of the removal of the sample's thermal history during the first heating[34]. The transition observed for TPTbP sample during the second heating cycle at 22.9 °C was attributed to some relaxation effects of the polymer chain. A melting of the hard segments is observed for the reference samples during 1st and 2nd heating. This may be related to the higher DPS value of these samples. Because HDI-based samples have a more ordered structure than Tolonate-based samples[28].

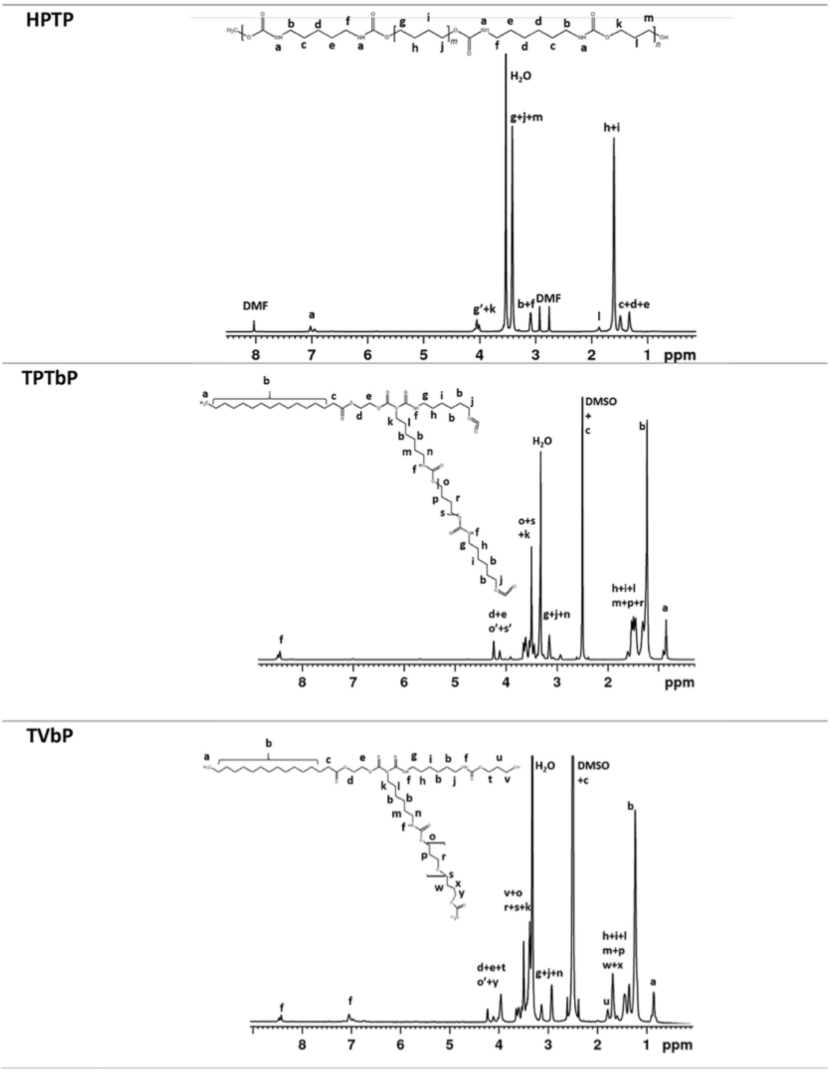

Table 4. ^1H nuclear magnetic resonance (NMR) spectra of the obtained samples in DMSO and DMF.

Thermogravimetry

TGA is used to measure thermal decomposition and thermal stability of materials. The TGA measurements were carried out on PUs based on both bio-based monomers and petrochemical feedstocks. The aim was to investigate the thermal stability of the prepared materials and to determine the influence of the bio-based substrates on the final properties of the product. The TG and DTG curves are shown in Figs. 7 and 8. Table 7 shows the temperatures for 5%, 50% and 90% mass loss and the ash residue in mass % at 600 °C.

As it can be observed all samples exhibited two steps of degradation. The first step is attributed to the decomposition of HS, including mainly isocyanate residues and chain extenders. This is caused by the relatively

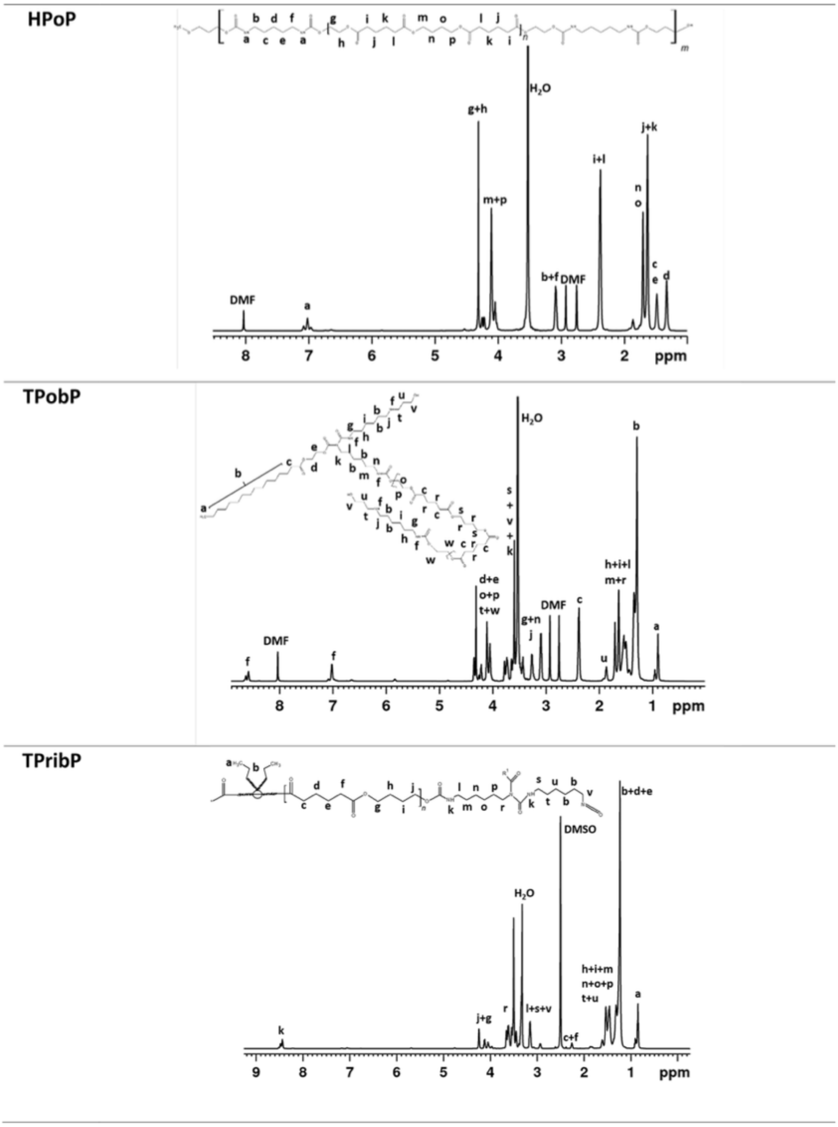

Figure 4. (continued)

low thermal stability of the urethane groups[35]. In contrast, the second step is attributed to the decomposition of SS, which is mainly composed of long polyol chains.

From the TG curves, it was observed that they are almost superposed, while the DTG curves are only partially overlapped. The bio-based PUs are slightly less stable than the reference samples because their initial decomposition temperature is lower (see Table 7).

The temperatures for the first step of mass loss are similar, ranging from 237 °C to 248 °C for samples based on polyester, and 238–251 °C for samples based on polyether. Therefore, we can conclude that polyether-

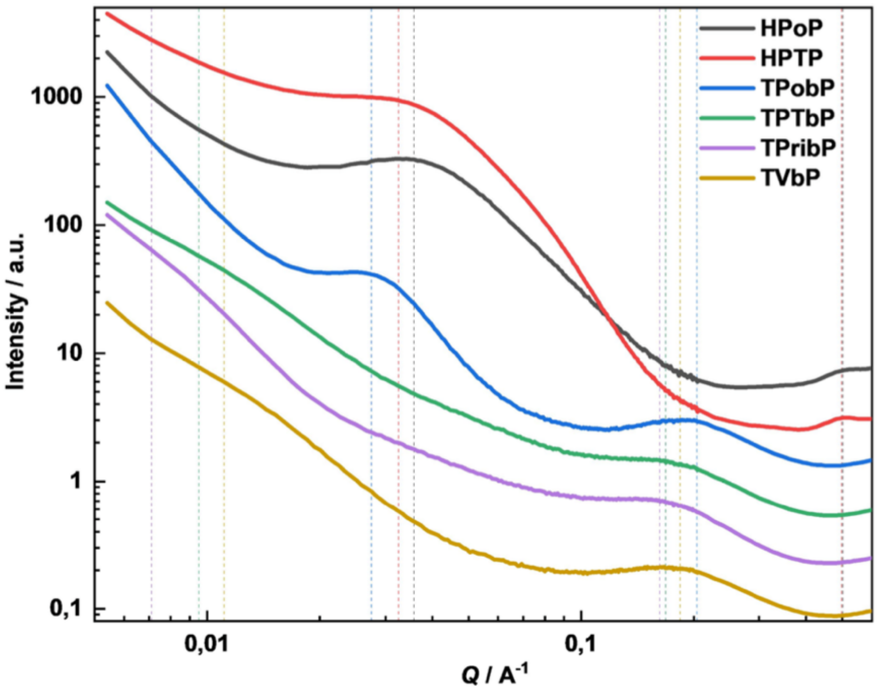

Fig. 3. SAXS curves of PUs. Vertical lines indicate the positions of peaks.

	Peak 1 – microphase separation		Peak 2 – structure of hard segments	
Sample code	Q/A^{-1}	d/nm	Q/A^{-1}	d/nm
HPoP	0.0357	17.6	0.502	1.3
HPTP	0.0325	19.3	0.498	1.3
TPobP	0.0275	22.8	0.204	3.1
TPTbP	0.0095	66.1	0.168	3.7
TPribP	0.0071	89.1	0.162	3.9
TVbP	0.0111	56.6	0.184	3.4

Table 5. SAXS peak positions and corresponding sizes of structural elements.

based samples are more stable than those on polyester. This is related to the different structures of the polyols (symmetrical and short chain of Velvetol and PTMG, long chain of Polios, branched chain of Priplast). Furthermore, it can be observed that PUs derived from bio-isocyanates degraded at a lower temperature than those based on petrochemical HDI. For comparison, 5% weight loss of HPTP sample occurs at $T=297$ °C, and TPTbP sample at $T=284$ °C. This is related to the lower thermal stability of bio-based isocyanate compared to the stability of HDI. As the thermal stability of isocyanates is closely related to the symmetry of their structure[27]. When the symmetry of the isocyanate increases, the stability of the PU increases, so Tolonate X FLO 100 has a lower stability due to its branched structure. However, our Tolonate-based samples had only slightly lower thermal stability than those reported by other scientists, also based on Tolonate and Velvetol (with a different polyol mass, we used 2000 g/mol versus 500 g/mol), where the $T_{5\%}$ was 292 °C[19].

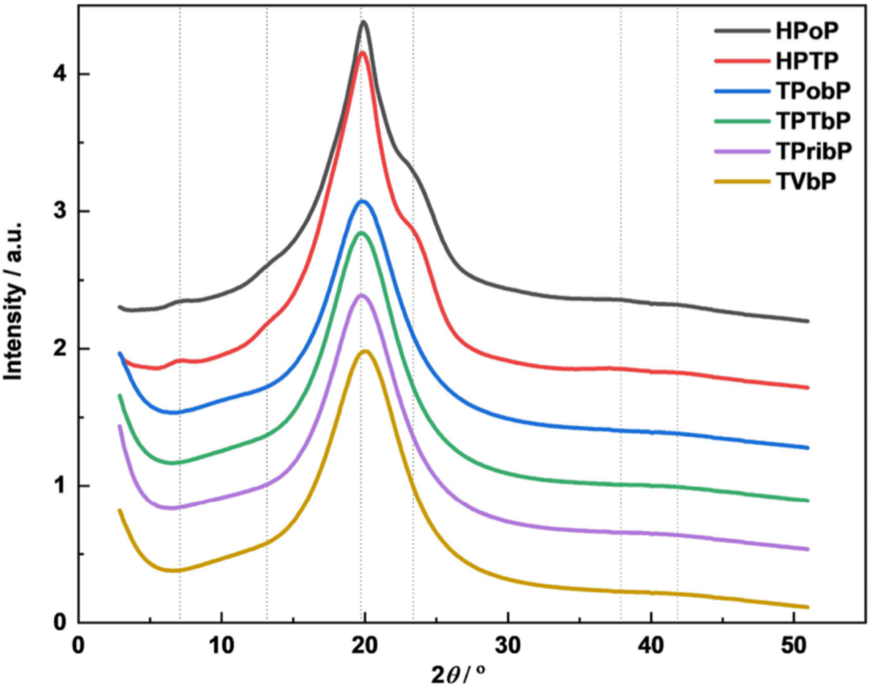

Fig. 4. WAXS curves of PUs. Vertical lines indicate the positions of peaks.

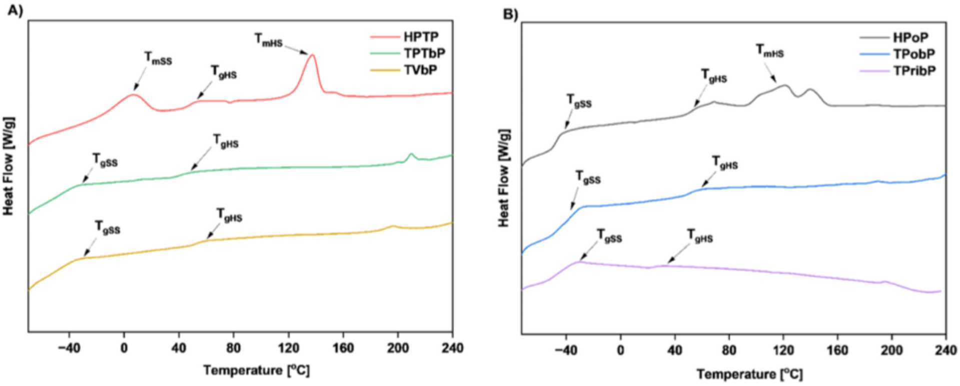

Fig. 5. DSC curves (first heating) of the obtained PUs: (**A**) based on polyether polyol (**B**) based on polyester polyol.

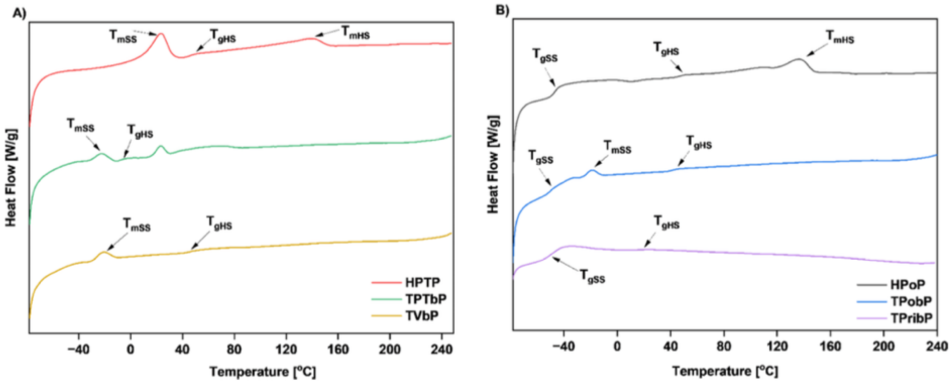

Fig. 6. DSC curves (second heating) of the obtained PUs: (**A**) based on polyether polyol (**B**) based on polyester polyol.

Sample code	Soft Phase T_{gSS}/°C	Hard Phase T_{gHS}/°C	Soft Phase Melting/°C	Hard Phase Melting/°C	$\Delta H/Jg^{-1}$ (melting SS/ melting HS)
HPTP	-	46.9	23.1	141.8	25.96/4.89
TPTbP	-	-	-22	-	4.49/3.46
TVbP	-	45.4	-21.8	-	4.35/ -
HPoP	-47.4	46.9	-	136.5	9.09/ -
TPobP	-47.4	41.1	-19.3	-	2.35/ -
TPribP	-55	18.1	-	-	-

Table 6. Thermal properties of the samples determined by DSC (2nd heating).

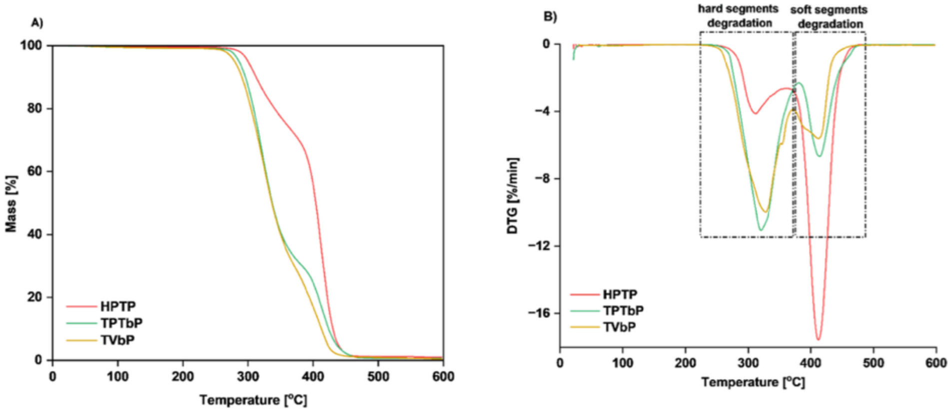

Fig. 7. TG and DTG curves of polyether-based PUs. (**A**) TG; (**B**) DTG.

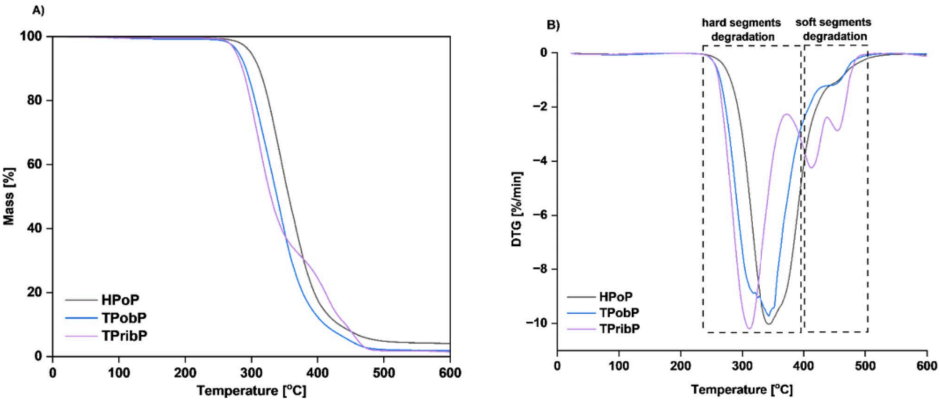

Fig. 8. TG and DTG curves of polyester-based PUs. (**A**) TG; (**B**) DTG.

Sample code	$T_{d5\%}$ [°C]	$T_{d50\%}$ [°C]	$T_{d90\%}$ [°C]	Char residue [%]
HPTP	297	403	429	0.94
TPTbP	284	336	423	0.53
TVbP	278	330	407	0.41
HPoP	295	355	426	4.0
TPobP	277	338	406	1.8
TPribP	274	328	437	1.38

Table 7. Temperature values at different mass losses [%]. $T_{d5\%}$ is the temperature of 5% mass loss, $T_{d50\%}$ is the temperature of 50% mass loss and $T_{d90\%}$ is the temperature of 90% mass loss.

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy

The gases produced during TGA of the samples at different temperatures (50–800 °C) were analyzed by FTIR spectroscopy. Analysis of the spectra of volatile decomposition products confirmed the relationships presented in the TGA figures. Decomposition of HS occurs in the first step and, according to the literature, leads to the formation of isocyanate and alcohol, primary or secondary amine, olefin, and carbon dioxide[8,36]. Meanwhile, in the second step, decomposition of SS consisting of polyols occurs. Temperatures in the range of 343–429 °C were chosen as the most representative points to illustrate characteristic groups of gas products.

All of the FTIR spectra shown in Fig. 9 exhibit absorption bands typical of carbon dioxide, at a wavenumber in the range 2391–2344 cm^{-1}, associated with asymmetric stretching vibrations, at 696–668 cm^{-1}, attributed to degenerate bending vibrations, and at 3598–3350 cm^{-1} corresponding to combination bands. The spectrum also reveals bands at 2941–2928 cm^{-1} and 2865–2849 cm^{-1}, characteristic of asymmetric and symmetric C-H stretching vibrations, and at 1479–1450 cm^{-1}, characteristic of asymmetric and symmetric C-H bending vibrations, of methylene and methyl groups.

The presence of a band at 1060–1067 cm^{-1} confirms the formation of primary alcohols, associated with C-O stretching vibrations, and at 3649 –3626 cm^{-1}, associated with O-H stretching vibrations.

Dynamic mechanical and thermal analysis

The DMTA results show us the supramolecular arrangement of prepared PUs (Fig. 10). The storage modulus curves clearly indicated the main transition in the range of ca. -68 – -28 °C corresponding to the glass transition temperature of SS. From the maximum of the tan delta curves, the main (alpha) temperature (T_α) of SS was determined to be of -34 °C for polyether-based (TPTbP and TVbP) and − 28 °C for polyester-based (TPobP and TPribP) bio-PUs, while the T_α values of the reference samples based on HDI were slightly lower, -68 °C and − 44 °C for HPTP and HPoP, respectively.

The PU materials based on the bio-based isocyanate Tolonate X FLO 100 were generally more flexible than the materials based on HDI, because in the SS transition region their storage modulus drops sharply by 3 orders of magnitude (from GPa units to MPa units). The subsequent slower decrease of the storage modulus at temperatures above about 0 °C may be related to the melting of crystalline domains, or to Tg of HS. In contrast, the HDI-based PUs were much stiffer materials, as the storage modulus in the transition region of SS only decreased by one order of magnitude. Then there was a gradual decrease of the storage module up to a

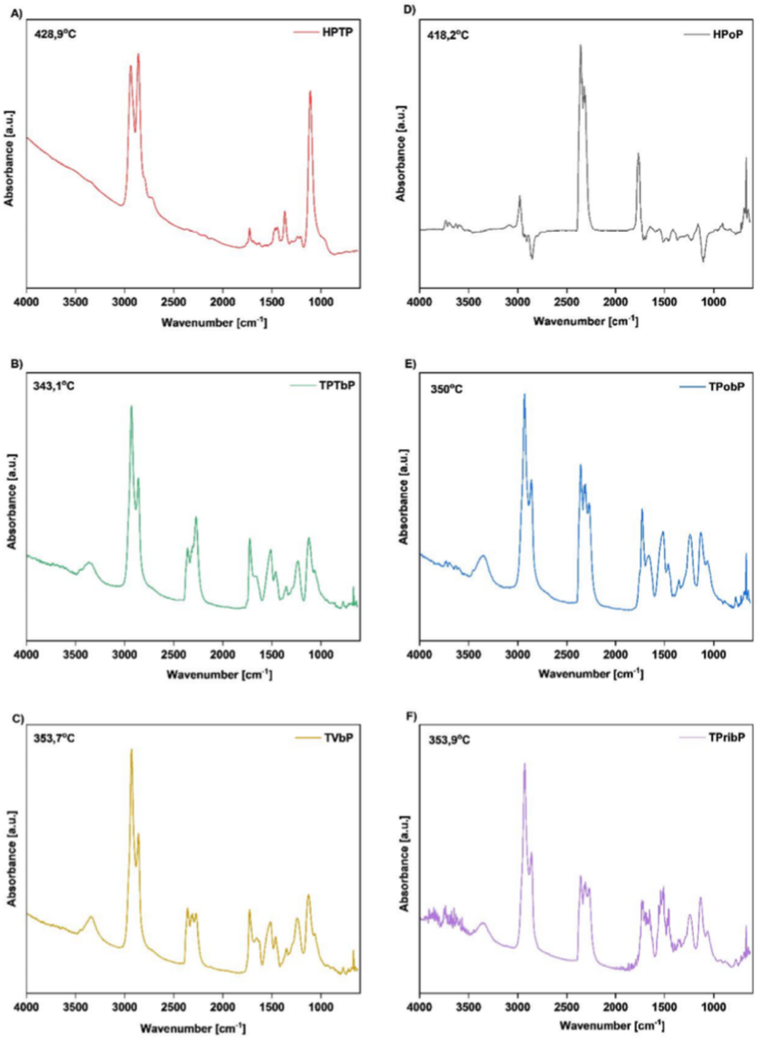

Fig. 9. FTIR spectra of the obtained PU: (**A**) HPTP, (**B**) TPTbP, (**C**) TVbP, (**D**) HPoP, (**E**) TPobP, (**F**) TPribP at various temperature points.

temperature of about 25 °C, which may be related to the melting of the crystalline phase (see the DSC results above). However, the HDI-derived samples are overall more segregated into SS and HS domains than the bio-based PUs, which was manifested by a significant sharp drop in the storage modulus at temperatures of approx. 120 °C (HPoP) and 130 °C (HPTP), related to the melting of crystalline domains in HS.

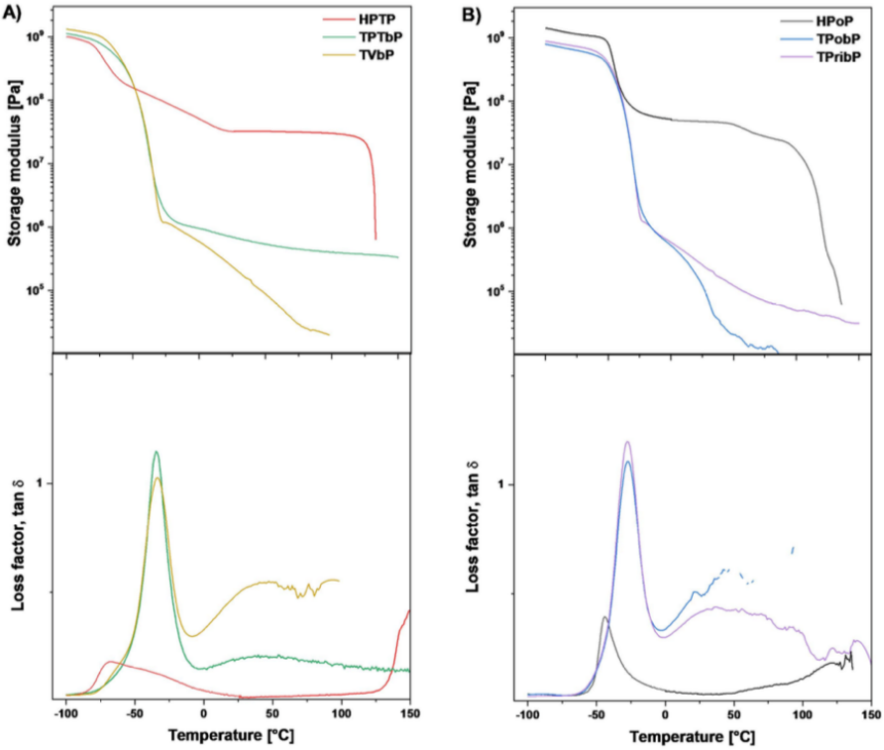

Fig. 10. DMTA results of PUs based polyether (**A**) and polyester (**B**) polyols.

Conclusions

A series of samples containing from 0 wt% to 52 wt% green carbon were prepared. The high green carbon content had no negative effect on the synthesis of the PUs. Samples of both petrochemical and bio-based monomer were prepared using the same method under similar conditions. For bio-based samples, lower curing temperatures could be applied, which is economically beneficial. The structure of the samples obtained was confirmed by FTIR and NMR analysis. The presence of characteristic functional groups and the complete rearrangement of the monomers were confirmed. It was also observed that the materials obtained from petrochemical monomers have a higher degree of phase separation. The SAXS profiles of all PU samples show two distinct peaks, indicating microphase separation and periodic structures in the hard segments. The HDI based samples show peaks at higher Q values, indicating a more compact structure with smaller domain. Bio-PUs were characterized by a reduced intensity of the second peak, suggesting that they have reduced crystallinity or less defined hard segment domains. TG analysis showed that the bio-based PUs were slightly less stable than the reference samples due to their lower initial decomposition temperature. Based on DSC, we confirmed the observations from WAXS, as melting peaks were observed only for the reference samples, confirming their crystalline fraction. However, for the bio-PU samples, glass transition temperatures were observed for the hard and soft segments, depending on the morphology of the samples. The DMTA results show that bio-based polyurethanes are generally more flexible than HDI-based ones, with a sharp decrease in storage modulus in the soft segment (SS) transition region. The T_α of the SS was higher for polyester-based (-28 °C) than for polyether-based (-34 °C) bio-PUs, while HDI-based samples showed even lower T_α values. The HDI-based PUs were stiffer, with a more gradual modulus decrease and distinct melting transitions at higher temperatures.

Data availability

The datasets used and analysed during the current study available from the corresponding author on reasonable request.

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Author contributions

J.B. wrote the main manuscript text.J.B. prepared the FTIR, DSC, TG, TG-FTIR analysis. R.K. prepared the NMR analysis.V.P. prepared the SAXS and WAXS analysis.H. B. prepared the DMTA analysis.J.D. and H.B. provided expert support.All authors reviewed the manuscript.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

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Co-authors’ statements of contribution:

Gdańsk, 07.03.2025 r.

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DECLARATION

As a co-author of the following publications:

1. Niesiobędzka, J., & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.

2. Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.

3. Brzoska, J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.

4. Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of providing consultation during the execution of the experimental work, evaluating the literature review, and proofreading the papers. Therefore, my contribution to the above-mentioned publications is as follows:

1. 30%

2. 15%

3. 15%

4. 10%

……………………………………….

Date and signature

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1. **Brzoska,** J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.

which is part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of providing consultation during the execution of the experimental work, conducting a DMTA analysis, and proofreading the paper. Accordingly, my contribution to the aforementioned publication amounts to 15%.

6.12.2024

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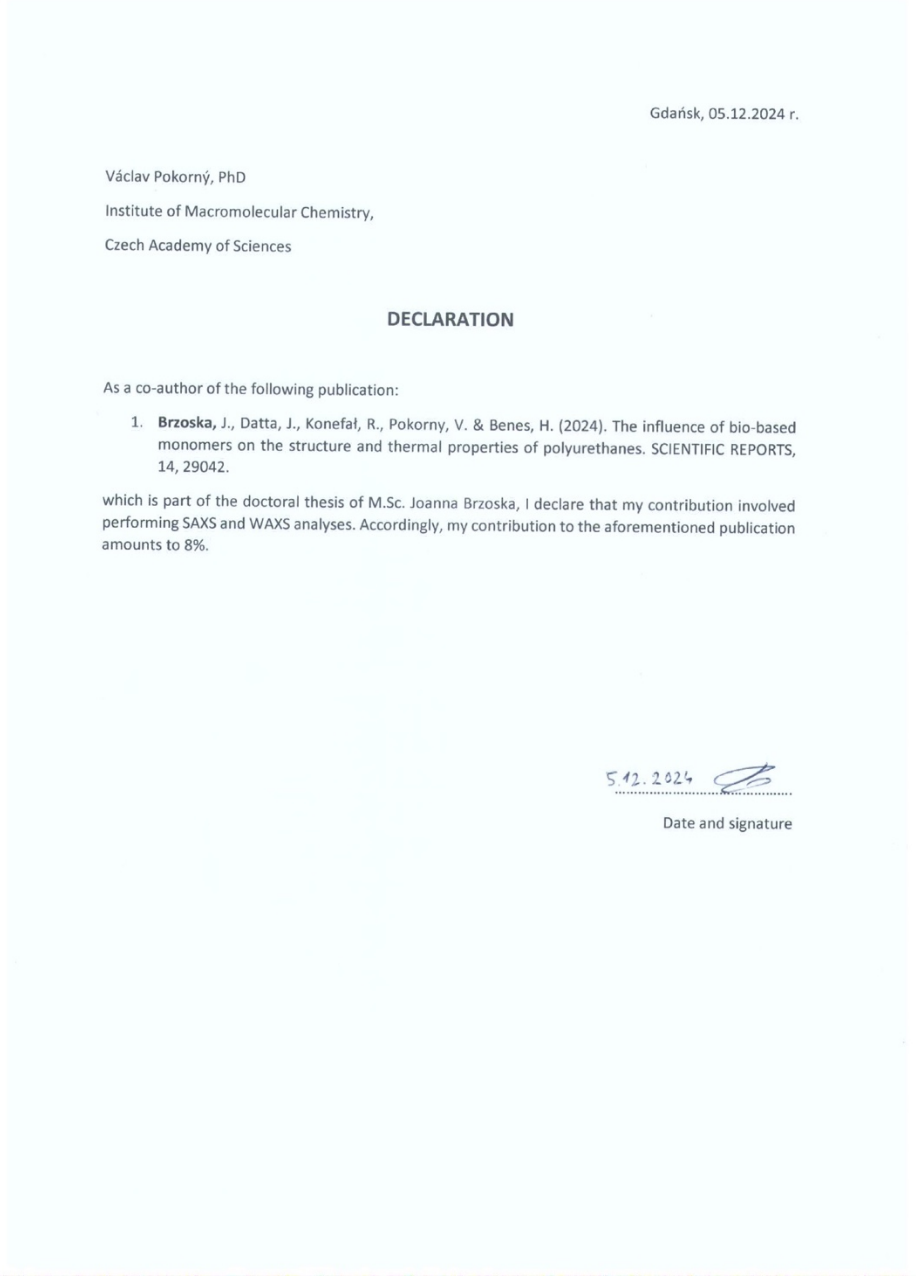
Date and signature



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which is part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution involved performing SAXS and WAXS analyses. Accordingly, my contribution to the aforementioned publication amounts to 8%.

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which is part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution involved performing NMR analyses. Accordingly, my contribution to the aforementioned publication amounts to 8%.

06.12.2024

Date and signature

3.4. Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.	
Article title	A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates
Author's contribution	I was responsible for preparing a significant portion of the manuscript. I designed and carried out the syntheses described in the publication. I conducted analyses of the chemical structures and properties of the obtained materials, such as FTIR, TGA, DSC, DMTA, mechanical tests, hardness, and swelling, while I was responsible for describing the results of the FTIR, DSC, XRD, and swelling measurements.
Percentage contribution	**Joanna Brzoska** **40%** Joanna Smorawska 15% Ewa Głowińska 35% Janusz Datta 10%

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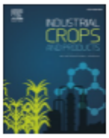

A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates

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ABSTRACT

The need for sustainability and a circular economy leads to the development of innovative greener materials and technologies. This paper is focused on a novel class of bio-based polyurethanes (PUs) synthesized with the use of bio-monomers including bio-based isocyanates. The novelty of this work is related to the usage of bio-based modified isocyanate via a two-step solvent-free synthesis of novel cast bio-based poly(ester-urethanes) and poly(ether-urethanes). The designed and prepared bio-based PUs were analysed in terms of their chemical structure, thermal stability, mechanical and thermomechanical properties. Fourier transform infrared spectroscopy confirmed the formation of urethane groups and allowed the calculation of the carbonyl index and the degree of phase separation. Differential scanning calorimetry and X-ray diffraction indicated the amorphous behavior of the obtained bio-based materials. It was established that not only the thermal stability but also the degradation steps depended on the structure of the hard segments and the phase separation between hard and soft segments. The modification of hard segments was also revealed in the results of thermomechanical and mechanical behavior of bio-PU which indicated a mixed phase structure.

1. Introduction

Advances in polymer science and the use of renewable resources for their synthesis have led to the industrial-scale availability of bio-based polymers and monomers. The replacement of fossil carbon in the synthesis of plastics with renewable carbon from biomass creates an alternative solution to conventional plastics production. According to the literature, the global bio-based polymer market will be constantly growing. Up to 2028 it is estimated to reach US$ 10.9 Billion (Grand View Research, 2021). Owing to that, bio-based polymers could find an application in everyday life products. This would not be possible without developments in the synthesis of bio-based monomers.

Bio-based monomers and compounds are the reason behind a significant development also in polyurethane chemistry and processing. Currently, polyurethanes can be produced based almost totally on sustainable compounds, e.g. the ones derived from plants or resulting from recycling. Bio-based polyurethanes are mostly synthesized by using bio-based polyols, bio-glycols, and petrochemical di/polyisocyanates. Nowadays, the biggest challenge in bio-based polyurethane synthesis is the replacement of petrochemical isocyanate components (Niesiobędzka and Datta, 2023). Although scientific progress has been made, challenges remain in terms of availability, production costs and scaling up to industrial scale. The use of bio-based isocyanates is important for sustainability as it will lead to the creation of products that are less dependent on petrochemical feedstocks, reduce greenhouse gas emissions and contribute to greener production. However, a good way to optimize the use of available raw materials is to modify them according to product requirements. In the synthesis of isocyanates, modifiers of natural origin can be used to achieve specific properties, such as reactivity, solubility, and thermal or mechanical properties (Głowińska et al., 2021).

There are several modifiers that can be used in the production of polyurethanes. Some of them are of biological origin. Due to high reactivity of the isocyanate groups, especially in contact with atmospheric moisture, it is desirable to modify them to prevent undesirable side reactions of the isocyanates. This is done by blocking the functional groups in the isocyanate. On the other hand, the incorporation of a blocking agent into the isocyanate structure leads to an improvement of the properties of PUs. Knospe et al. suggested blocking the isocyanate (HDI trimer) with vanillin. The authors point out the advantages of using vanillin, such as the low unblocking temperature and non-toxicity (Knospe et al., 2022). Meanwhile, in her research, P. Kasprzyk

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chemically modified Desmodur eco N7300 triisocyanate to a difunctional monomer (mPDI) using ethanol (Kasprzyk, 2020). The modification reaction was carried out at 60 °C for 2 h in a nitrogen atmosphere. The obtained diisocyanate (mPDI) was used in a polyaddition reaction to synthesize modified polyurethanes. It was found that the polyurethanes prepared with mPDI had similar thermal stability to those synthesized with MDI (methylene diphenyl diisocyanate, petrochemical). Furthermore, the thermoplastic polyurethanes obtained from the modified isocyanate were characterized by high acoustic and mechanical damping. Cardanol (a phenol derivative of biological origin), produced from cashew nut shell liquid (CNSL), is another interesting modifier of isocyanate groups (Caillol, 2018; Ike et al., 2021). The unique structural properties, high availability, low cost and inedibility (no competition with the food industry) make it an interesting raw material (Denis et al., 2022). The Cardolite corporation offers a commercially available product, Cardolite NX-2026, which is a universal modifier derived from cardanol. As the manufacturer declares, the product is characterized by high purity, low odor, lighter color and accelerator for use in coatings (Cardolite company, 2018).

Bio-based polyurethanes made from natural raw materials have properties that may differ from those of conventional polyurethanes made from petrochemical raw materials. First of all, depending on their chemical composition, bio-based polyurethanes can be biodegradable and can reduce the negative impact of plastics on the environment by reducing greenhouse gas emissions. Secondly, bio-polyurethanes can have similar mechanical properties (tensile strength, hardness) and thermal properties compared to petrochemical polyurethanes.

In the literature, plenty of scientific articles regarding bio-based polyurethanes may be found. Nevertheless, there is still a lack of knowledge of functionalized bio-based isocyanates and their influence on PU structure and properties. In this work, we propose the use of bio-based monomers and their implementation for the two-step synthesis of polyurethanes. For the first time, an isocyanate group bio-based modifier was used to increase the green carbon content and alter the functionality of the isocyanate. The use of the isocyanate group modifier allowed us to obtain cast polyurethane elastomers from a trifunctional isocyanate. This is the first paper to demonstrate the possibility of isocyanate modification while at the same time increasing the number of bio-based segments. Solvent-free synthesis led us to prepare 2 series of polyurethanes, based on bio-based polyols and petrochemical polyol. The main idea of this work is presented in the diagram below (Fig. 1).

2. Methods of characterization

2.1. Fourier transform infrared spectroscopy

The chemical structure of the bio-based polyurethane was analysed by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 8700 spectrophotometer with universal ATR accessory (Thermo Electron Corporation, USA). Spectra were recorded at room temperature for a wavenumber range of 500–4500 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was acquired with 64 scans.

The degree of the carbonyl groups participating in hydrogen bonding can be described by the carbonyl hydrogen bonding index, R, as given in Eq. (1),

$$R = \frac{A_{H-bonded}}{A_{H-free}} \tag{1}$$

where A is the intensity of the characteristic absorbance ($A_{H\text{-bonded}}$ – absorption intensity of hydrogen-bonded carbonyl; $A_{H\text{-free}}$ – absorption intensity of free carbonyl). The degree of phase separation (DPS) and the degree of phase mixing (DPM) can be obtained by using Eqs. (2) and (3), respectively.

$$DPS = \frac{R}{R+1} \tag{2}$$

$$DPM = 1 - DPS \tag{3}$$

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the substrates and polyurethanes was performed using a NETZSCH DSC 204F1 Phoenix Analyzer. Approximately 10 mg of the sample was placed in a ceramic crucible and heated from 35 to 600 °C at a heating rate of 10 °C/min under a nitrogen flow of 20 mL/min.

2.3. Differential scanning calorimetry

The thermal behavior of the polyurethanes was evaluated by differential scanning calorimetry (DSC) using a TG 209F1 Libra (NETZSCH, Germany). The samples (5–10 mg) were encapsulated in aluminum hermetic pans. The measurements were carried out in a heating-cooling-heating cycle at the temperature range of (-80) – 250 °C. The analyses were performed at a heating rate of 10 °C/min in an inert (nitrogen) atmosphere.

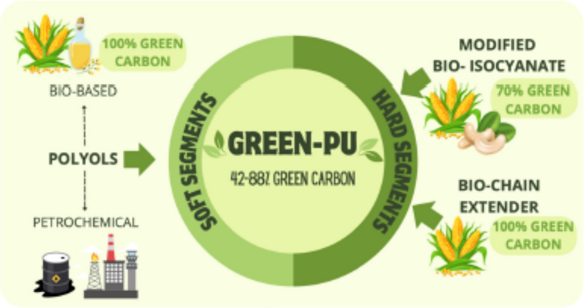

Fig. 1. The building components of the obtained green polyurethanes, their type and origin. The use of increased amounts of bio-based reagents makes these materials safer for the environment.

2.4. *Dynamic mechanical analysis*

The dynamic mechanical analysis was carried out by using a TA Instrument DMA Q800. This test was conducted with the use of rectangular-shaped samples (40x10x2 mm). The samples were heated at 3°C/min at a temperature range of – 100–150°C, using a constant frequency of 10 Hz.

2.5. *X-ray diffraction (XRD)*

X-ray diffraction was conducted with a Phillips X'Pert Pro diffractometer (XRD, Panalytical, Almelo, Netherlands) with CuKα radiation (1.540 Å). The measurements were performed at 40 kV and 30 mA at room temperature. The diffraction angle of 2Θ ranged from 10° to 60°.

2.6. *Mechanical properties*

Tensile testing was carried out at room temperature with a Zwick/Roell Z020 universal testing machine with cross-head speed 100 mm/min, in accordance with ISO 37. Dumbbell-shaped samples (type 5A) with a gauge length of 25 mm were tested.

2.7. *Hardness*

Hardness was measured using an electronic Shore Durometer type A at room temperature, according to ISO 868. The results are the average of 10 measurements carried out for each sample.

2.8. *Density*

Density was determined according to the PN-EN ISO 1183–1:2013–06 standard. The measurements were performed in methanol at ambient temperature. The results are the average of 5 measurements carried out for each type of material.

2.9. *Swelling*

Swelling measurements of the obtained samples were carried out at room temperature using two different solvents (toluene and acetone). Swelling tests were performed on 10 x 10 mm samples. Each sample was placed into a cup filled with 4 mL of solvent, covering the entire surface. Three tests were performed for each sample. Periodically, these samples were removed from the solvent and weighed after removing the excess of the solvent from the sample using filter paper. This was repeated until a constant weight was obtained (equilibrium swelling). The samples were then air-dried for two days and dried in a laboratory oven at 80°C until a constant weight was reached. The average value from three parallel swelling experiments in each solvent for each sample was used.

The swelling ratio (SR) is the mass of solvent (m_{as}) that was absorbed by the sample divided by the initial mass of the sample (m_{is}). The mass of the absorbed solvent was determined as the difference between the mass of the sample after (m_{ss}) and before the swelling test (m_{is}). The swelling factor was determined using Eq. (4) as follows:

$$SR = \frac{m_{ss} - m_{is}}{m_{is}} = \frac{m_{as}}{m_{is}} \tag{4}$$

3. Experimental part

3.1. *Materials*

For the preparation of PU samples four types of polyols were used. Two types of polyether polyols: poly(tetramethylene glycol) (PTMG) supplied from Overlack (Ozorków, Poland) and bio-based poly-propanediol (PO3G – Velvetol H2000) supplied from Allessa (Frankfurt, Germany), and two types of polyester polyols: α,ω-oligo(ethylene-butylene adipate)diol (Polios 55/20) purchased from Purinova (Bydgoszcz Poland) and bio-based semicrystalline Priplast 3294™ supplied by Croda (Snaith, UK). All of the polyols had the same molecular weight of ~2000 g/mol. A partially bio-based product with the trade name Desmodur eco N 7300 supplied by Covestro (Leverkusen, Germany) was used as an isocyanate. Moreover, Cardolite® NX-2026 supplied by Cardolite Corporation (Pennsylvania, USA) was used as a modifier for the isocyanate trimer. The chain extender Zemea (1,3-propanediol) was purchased from DuPont Tate & Lyle Bio Product (Naucalpan de Juárez, USA). The catalyst, dibutyltin dilaurate (DBTDL), was purchased from Sigma Aldrich (Saint Louis, USA). The reaction inhibitor was orthophosphoric acid supplied by POCH Gliwice (Gliwice, Poland). The chemicals were used without further purification unless stated otherwise. Fig. 2 shows a diagram for the preparation of green polyurethanes.

3.2. *Synthesis of polyurethane elastomers*

Polyurethanes were obtained using a two-step prepolymer method. First, the polyol and chain extender were degassed and dehydrated at 95 °C under vacuum for 1 h. In the next step, the isocyanate modification reaction was conducted using -NCO group blocker – CARDOLITE. The reactions were carried out in a four-neck round-bottom flask at about 60 °C in a nitrogen atmosphere for 1 h. Then the prepolymer was obtained by reacting the selected polyol with an excess of modified isocyanate at 85 °C for 2 h in a nitrogen atmosphere. During the reaction, the percentage of NCO groups was determined by titration according to ISO 14896:2010. Subsequently, a chain extender and a catalyst (0.1 wt% DBTDL) were added to the prepolymer, and the mixture was stirred for 30 s and degassed under vacuum for 60 s. The molar ratio of [NCO]/[OH] groups was 1.05. Finally, the materials were cured in a laboratory oven at 60–80 °C up to 48 h. Table 1 present an example of sample formulation and Table 2 shows the characteristics of the samples. The samples were highly transparent and soft, indicating the possible amorphous nature of bio-based polyurethanes, which was later confirmed in this work.

3.3. *Fourier transform infrared spectroscopy*

The chemical structure of the obtained PU materials was investigated with the use of Fourier transform infrared spectroscopy (Fig. 3). The FTIR spectra confirmed the correct route of polymerization with the formation of a urethane bond. In all samples, a band corresponding to the N-H bond was observed at the range of 3370–3339 cm^{-1}, confirming the presence of a urethane group in all samples. The absence of a band between 2300 and 2200 cm^{-1}, characteristic of the isocyanate group, indicates that the substrates have been completely reacted. A band in the range of 1691–1681 cm^{-1} of isocyanurate skeleton is also observed for all samples (Morales-Cerrada et al., 2021). The next important bands are: stretching vibrations of C–O–C in ether bonds (1100 cm^{-1}, introduced by ether-based polyol) and in ester bonds (1243–1233 cm^{-1}, introduced by ester-based polyol). The bands observed between 2923 and 2854 cm^{-1} are ascribed to symmetric and asymmetric stretching of the C-H bond with the carbonyl.

Decomposition of the carbonyl peak (Fig. 4) enabled the determination of the degree of phase separation (DPS) and the degree of phase mixing (DPM) based on the carbonyl index (R). The obtained values of R, DPS and DPM for PU samples were given in Table 3. Based on FTIR spectra and decomposition of peaks associated with carbonyl -C=O groups, it was calculated that the degree of phase separation showed higher values than the degree of phase mixing. The contribution of hard segments is a relative measure of the degree of phase separation in PU. If the percentage of hard segments increases, the degree of phase separation decreases. The materials are characterized by efficient phase separation, reaching over 50 % for the sample based on Polios, and over 70 % for the other samples. Minor differences in the position of carbonyl

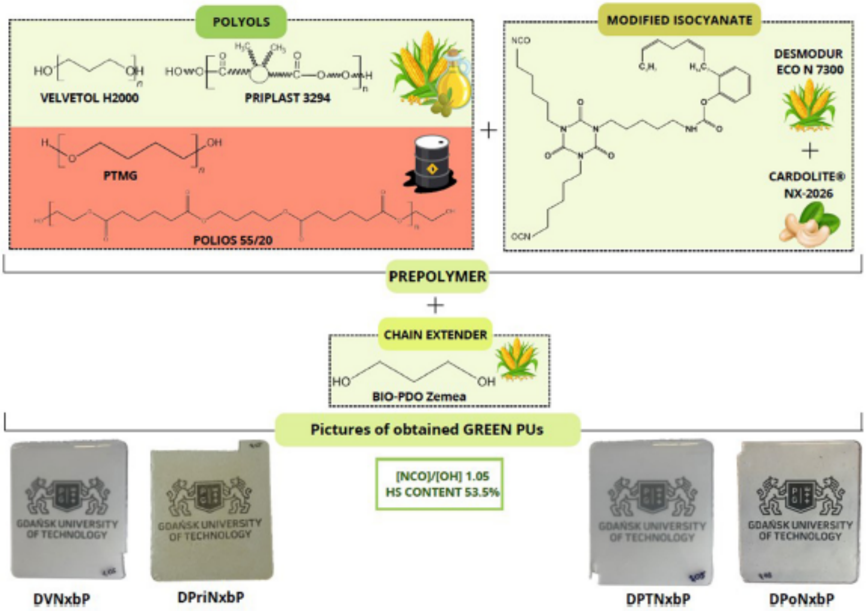

Fig. 2. Diagram presenting the preparation of green polyurethanes. Pictures of the synthesized samples show their transparent character.

Table 1
Example of a polyurethane formulation.

Polyol [g]	Isocyanate [g]	Chain extender [g]	Modified [g]	Catalyst [g]	Inhibitor [g]
116.12	88.35	2.93	45.03	0.003	0.0038

peaks were observed for all PU samples, indicating their similarity. The DPTNxbP sample has the highest degree of phase separation between hard and soft segments, which implies that it has the highest number of hydrogen bonds in the range of hard segments.

3.4. *Thermogravimetric analysis*

The thermal stability of polyurethanes is one of the key properties of this material in terms of its prospective implementation. It depends on a number of variables, including the composition of the material (segmented structure), the [NCO]/[OH] ratio, or the conditions and method of synthesis. Thermogravimetric analysis makes it possible to observe and analyse changes in material mass as a function of temperature. One of the most important parameters is therefore $T_{5\,\%}$, shown in Table 4, which indicates the onset of thermal degradation. The parameters $T_{50\,\%}$, $T_{90\,\%}$ of weight loss and ash residue in 600 °C are also presented. The TG and DTG curves of the obtained green polyurethanes are shown in Figs. 5 and 6. The effect of changes in the structure and character (polyester/polyether) of the polyol on the thermal stability of the bio-PUs was considered.

An analysis of the TG curves (Fig. 5.) and Table 4 show a wide range of values for the $T_{5\,\%}$ (257–299 °C). PUs based on bio-based polyols have good thermal stability compared to PUs based on conventional polyols of petrochemical origin. In particular, PUs based on polyether bio-polyol (Velvetol) show the highest degradation start temperature (299 °C). Peng et al. also observed the thermal stability of Velvetol-based PUs around 300 °C in their work (Peng et al., 2022). The authors compared Velvetol and PTMG based PUs, but obtained a similar $T_{5\,\%}$ for both. In our case, the PTMG-based PUs show significantly lower thermal stability, but this may be influenced by the different type of isocyanate used (the thermal stability of isocyanates decreases as their symmetry decreases). The linear structure of Velvetol polyol may have a positive effect on the thermal properties of bio-PUs. Quite high $T_{5\,\%}$ values are also observed for samples based on the polyester polyol (Polios) (272 °C) and the polyester bio-polyol (Priplast) (265 °C). In the case of Priplast, an important fact is its semi-crystallinity, which can positively influence

Table 2
Sample description: codes, substrates, molar ratios of [NCO]/[OH] groups and content of the hard segments (HS) in the materials.

Sample	Polyol	Isocyanate	Glycol	[NCO] / [OH]	HS content [%]	Bio-based carbon content [%]
DPTNxbP	PTMG	Desmodur eco N 7300	bio-PDO (Zemea)	1.05	53.5	44
DPoNxbP	Polios 55/20	Desmodur eco N 7300	bio-PDO (Zemea)	1.05	53.5	44
DVNxbP	Velvetol H2000	Desmodur eco N 7300	bio-PDO (Zemea)	1.05	53.5	88
DPriNxbP	Priplast 3294	Desmodur eco N 7300	bio-PDO (Zemea)	1.05	53.5	88

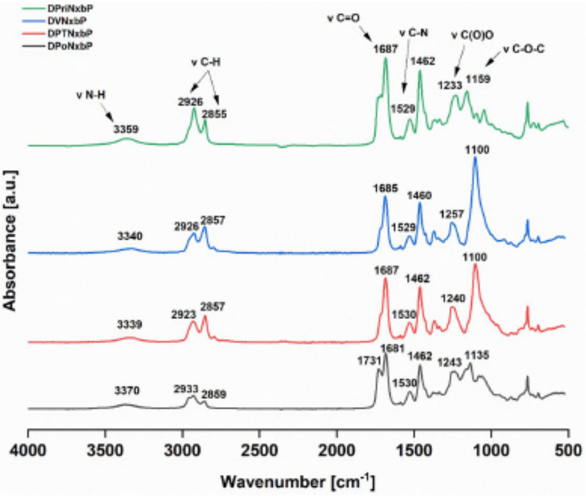

Fig. 5. FTIR spectra of PU samples obtained with different polyols: ether and ester polyols. The spectra were recorded at room temperature for a wavenumber range of 500–4500 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was acquired with 64 scans.

the phase separation in the material and explain the rather good thermal stability. There have also been reports in the literature that polyurethanes based on polyester polyols have a higher temperature resistance than polyether polyols (Carlos Quagliano Amado, 2020a). In our work, this cannot be unequivocally stated, due to the different structures of the polyols (symmetrical and short chain of Velvetol and PTMG, long chain of Polios, branched chain of Priplast), as well as the reaction with a modified isocyanate. The thermal stability of bio-polyurethanes developed using a modified isocyanate is comparable to that reported in other scientific reports on bio-based polyurethanes (Głowińska et al., 2024).

For the ash residue in 600 °C (see Table 4), the highest value are observed for the PU based on Polios. Generally, the differences in the residual rate are attributable to the chemical structure of the polyols used and the thermal resistance of the samples. It is well known that PUs based on polyester polyols exhibit greater thermal stability, resulting in a higher residual rate. On the other hand, thermal stability of PUs depends on morphology of the polyol. Based on the literature it can be conclude that the lower flexibility in chains of SS domains produced a lower thermal resistance threshold (temperature where 5 % sample weight is lost) as a result of lower crystallinity (Carlos Quagliano Amado, 2020b). That is why the highest residual rate was noted in the case of PU based on petrochemical polyester-polyol DPoNxbP series and much lower for PUs series DPriNxbP.

It is well known that polyurethanes degrade in two main stages: the first is the thermal decomposition of the hard segments and the second – of the soft segments. Fig. 6 shows the thermal degradation stages of the samples obtained. It can be seen that the stages are not clearly separated for the Polios and Priplast based samples. However, a complex degradation pathway is observed for both stages. This may be due to the phase mixing when degradation occurs over a wide temperature range.

3.5. *Differential scanning calorimetry*

The thermal properties of the obtained PU materials were studied using differential scanning calorimetry (DSC) and the results are presented in Fig. 7 and Table 5. DSC measurement enables determination of thermal properties and observation of crystallization and melting processes. From the registered DSC curve it is possible to determine the glass transition temperature of the soft and hard segments, the melting and crystallization temperatures, as well as to calculate the energy values (enthalpies) of the phase transformations.

For all samples, the glass transition temperature was observed for hard segments. Meanwhile, for the soft segments the glass transition temperature was only observed for the DPoNxbP sample. This is related to intermolecular interactions and morphological characteristics in the samples, which can lead to the absence of a distinct glass transition peak. Moreover, no melting points were recorded, indicating that all the samples have an amorphous and cross-linked structure. This may be due to the low molecular weight of polyols constituting soft segments, since they can no longer crystallize due to the restriction from the hard segments. Furthermore, blocked isocyanate, because of its asymmetrical structure, limited the susceptibility to crystallization of hard segments. The glass transition temperatures of the hard segments were similar, between 46 and 56 °C.

3.6. *Dynamic mechanical thermal analysis (DMA)*

Dynamic mechanical analysis leads to determining the viscoelastic behavior of polyurethanes. This thermal analysis method is useful to investigate and characterize the mechanical properties in the function of temperature. The viscoelastic behavior was studied in the temperature range from -100 °C to $+150$ °C. Based on the analysis of the results, the glass transition temperature of soft segments (T_{gSS}), the storage modulus E', the loss modulus E" and the loss factor tan(δ) were determined (Table 6). Analysing storage modulus curves (Fig. 8.), the effect of soft segment structure on thermomechanical bio-based PUs properties can be easily observed. Furthermore, the following characteristic of cross-linking materials was observed: the highest stiffness was exhibited by the following materials: DPoNxbP, based on petrochemical polyester polyol: α,ω-oligo(ethylene-butylene adipate)diol and DVNxbP, based on

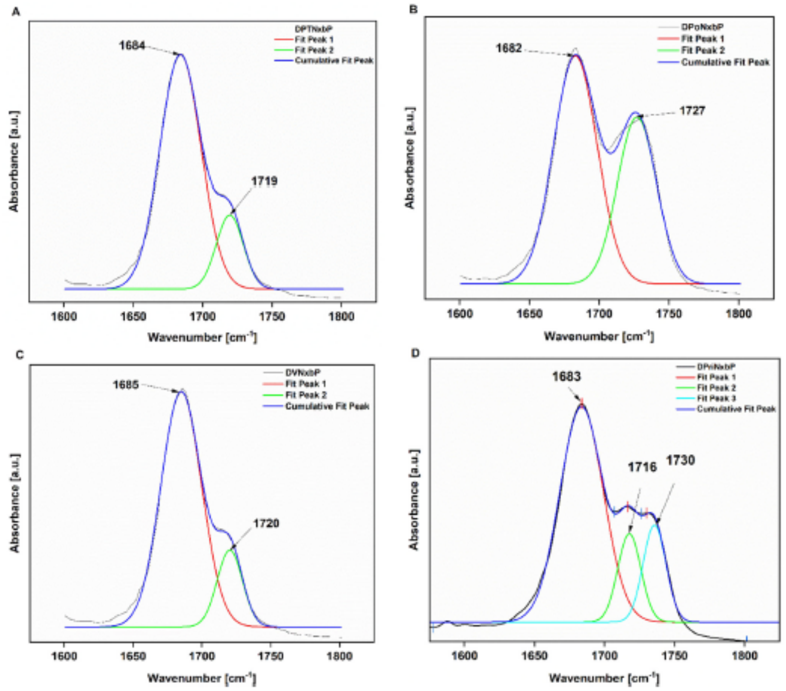

Fig. 4. Decomposition carbonyl peaks of polyurethane materials based on different bio-based monomers. Peaks at the lower wavenumber indicate the position of H-bonded carbonyl peak (ca. 1685 cm^{-1}), while the free carbonyl, which was assigned at ca. 1720 cm^{-1}, depends on the sample composition.

Table 3
The carbonyl hydrogen bonding index (R), the degree of the phase separation (DPS), and the degree of the phase mixing (DPM) in the prepared polyurethanes. A: absorption intensity calculated as the area of Gaussian multipeak fitting; * A_{bonded}: absorption intensity of hydrogen-bonded carbonyl; ** A_{free}: absorption intensity of free carbonyl.

Sample	A_{bonded}*	A_{free}^{**}	R	DPS	DPM
DPTNxbP	0.30851	0.10877	2.836	0.739	0.261
DPoNxbP	0.25764	0.19269	1.337	0.572	0.428
DVNxbP	0.27149	0.09869	2.750	0.734	0.266
DPriNxbP	0.66594	0.23235	2.866	0.741	0.259

Table 4
Thermal decomposition characteristics of the bio-based PUs. $T_{5\ \%}$ is the temperature of 5 % mass loss, $T_{50\ \%}$ is the temperature of 50 % mass loss and $T_{90\ \%}$ is the temperature of 90 % mass loss.

Sample	$T_{5\ \%}$ [°C]	$T_{50\ \%}$ [°C]	$T_{90\ \%}$ [°C]	Ash residue [%]
DPTNxbP	257	410	449	0.8
DPoNxbP	272	406	457	3.0
DVNxbP	299	419	461	1.1
DPriNxbP	265	415	463	1.1

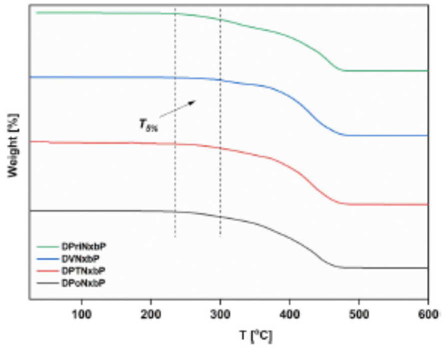

Fig. 5. TG curves of the obtained PUs, temperature program: heated from 35 °C to 600 °C with a heating rate of 10 °C/min, in a nitrogen atmosphere with a purge rate of 20 mL/minute. The temperature range of 5 % mass loss $T_{5\ \%}$ is marked with a dashed line.

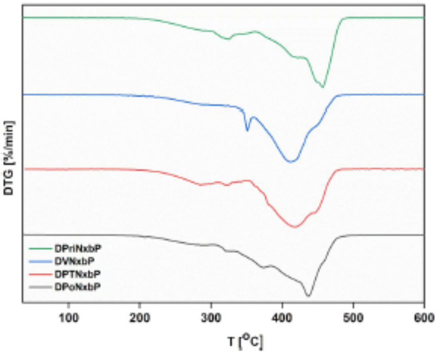

Fig. 6. DTG curves of the obtained PUs, temperature program: heated from 35 °C to 600 °C with a heating rate of 10 °C/min, in a nitrogen atmosphere with a purge rate of 20 mL/minute. The first and second main degradation steps are marked with a dashed line.

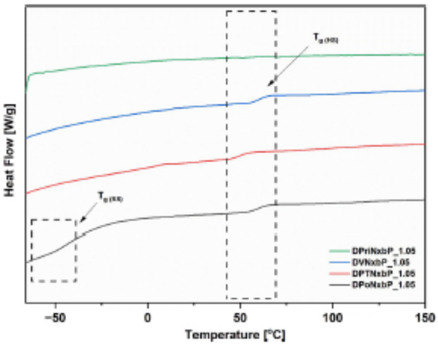

Fig. 7. Differential scanning calorimetry (DSC) curves for the obtained polyurethanes showing the characteristics of the second heating transitions.

Table 5

Glass transition temperatures of the soft and hard segments determined by differential scanning calorimetry from the second heating run.

Sample	T_{gSS} [°C]	T_{gHS} [°C]
DPTNxbP	-	46.4
DPoNxbP	–51.2	54.6
DVNxbP	-	56.3
DPriNxbP	-	49.5

Table 6

Thermomechanical characteristics of bio-based PU. The tanδ peak was used for the determination of Tg_{ss}.

Sample	E'_{max} [MPa]	$E'_{25°C}$ [MPa]	E''_{max} [MPa]	tanσ [-]	Tg_{ss} [°C]
DPoNxbP	5445	5.9	413	0.86	–2.1
DPTNxbP	707	5.9	173	0.34	–57
DVNxbP	3950	2.9	480	0.38	–52
DPriNxbP	2137	6.9	177	0.26	–37.7

bio-based polypropanediol. Considering logE' at room temperature (25 °C) the same trend might be noticed, which is related to the crosslinking share in the bio-PU structure.

Based on loss modulus curves (Fig. 8B), glass transition temperature of soft segments was determined. The highest T_{gSS} was noticed in the case of DPoNxbP materials, and it indicates a slightly crosslinked structure, which was also revealed in the swelling test. If we look at the tanδ curves, two phase alpha transitions can be observed – at the lower temperature related to soft segments, and at the higher temperature – to hard segments. Prima facie tanδ curves reveal mixed phase structure of DPriNxbP, DVNxbP and DPTNxbP materials that is closely related to the chemical structure of soft and hard segments. HS segments are dispersed in the soft phase. Taking into account tanδ values, all materials are characterized by good damping properties.

Regarding the petrochemical based polyols and their influence on thermomechanical properties, in the Fig. 8 B and C revealed weak transition at about –75 °C for DPTNxbP and – 60 °C for DPoNxbP which have usually been identified as the β-transition. According the literature β-transition is related to the movements of a chain section containing the urethane group attached to a crosslinker or to the motion of the backbone chain of the short groups in the fatty acid chains (Narine et al., 2007).

3.7. X-ray diffraction (XRD)

X-ray diffraction is a non-destructive technique used to analyse physical properties such as the crystal structure and phase composition of powder, solid and liquid samples (Nasrazadani and Hassani, 2016).

The XRD graph (Fig. 9) presents a comparison of the molecular structure of the samples with modified isocyanate and different polyols. All samples show a broad diffraction peak, indicating an amorphous structure, which is in line with the DSC analysis. The maximum of the diffraction peak is at an angle of about 20° (Table 7), which is similar to observations on polyurethanes made by other researchers (Fan and Chen, 2019; Hoseini and Nikje, 2018; Javaid et al., 2018).

3.8. Mechanical properties

The mechanical properties of PUs are closely linked to the composition of the hard and soft segments in a given material's macromolecular arrangement. Table 8 shows the values of the physico-mechanical properties, such as hardness, tensile strength, and elongation at break. Permanent elongation after break was also measured during the test, but it was unchanged for all samples, so its values were omitted. All the materials show a tensile strength in the range of 0.6–1.5 MPa. It is apparent that the highest strength characterizes the PTMG-based sample (1.5 MPa). This polyol contains evenly distributed carbons, which may favor better phase ordering. This may therefore positively influence the mechanical strength of the polyurethane. However, the differences are not pronounced when considering the standard deviation, but the tensile strength of the developed green polyurethanes is not high. Moreover, bio-based materials exhibit higher elongation at break compared to those derived from petrochemical polyols. This observation is consistent when comparing samples based on Priplast and Polios, as well as Velvetol and PTMG. The shorter chain length of Velvetol may contribute to increased chain mobility within the polyurethane matrix. Additionally, the side chains present in Priplast may enhance flexibility through a plasticizing effect, that is why PUs series DPriNxbP exhibit higher elongation at break in comparison to PUs series DPoNxbP.

The hardness of plastics is a property influenced by both the chemical structure and the degree of cross-linking, as well as the presence of other additives. Considering polyurethane materials hardness mainly depend on hard segments structure and occurrence of physical cross-linking by hydrogen bonds. Hardness is closely related to tensile strength. Analysing Table 8 we can noted that the hardness of samples

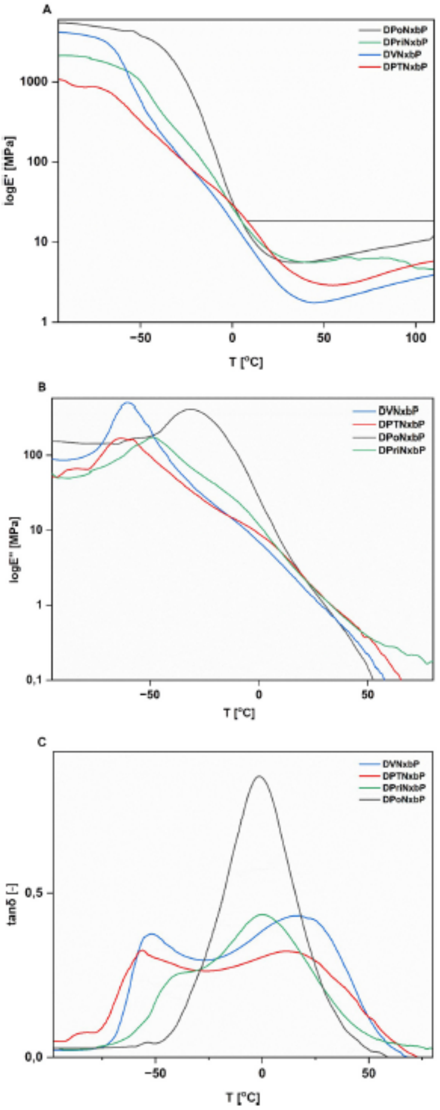

Fig. 8. DMA curves for the different bio-based PUs, where: A is storage modulus (E'), B is loss modulus (E'') and C is loss factor (tan δ) versus temperature.

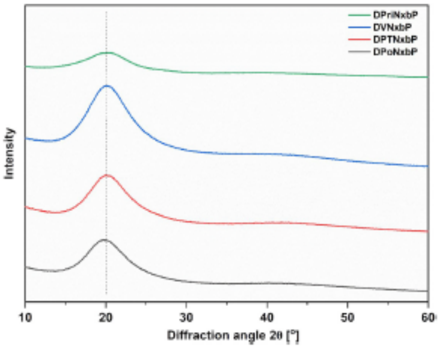

Fig. 9. X-ray diffractograms of polyurethane elastomers with different bio-based monomers.

Table 7
X-ray diffraction data with diffraction angles, relative intensities and percentages of hard segments of the obtained PUs.

Sample	2Θ [°]	Intensity	HS [%]
DPoNxbP	19.9	50,332	53.5
DPTNxbP	20.1	55,903	53.5
DVNxbP	20.1	76,945	53.5
DPriNxbP	20.3	22,913	53.5

Table 8
Mechanical characteristics of prepared samples.

Sample	Tensile strength [MPa]	Elongation at break [%]	Hardness [ShA]
DPoNxbP	0.6±0.1	35.7±6.4	48.3±0.5
DPTNxbP	1.5±0.4	83.2±26.6	56.8±0.6
DVNxbP	1.3±0.2	97.4±19.8	44.7±0.4
DPriNxbP	1.0±0.1	43.8±4.2	55.1±0.5

DVNxbP and DPoNxbP are similar, between 44.7 and 48.3, as are the hardness of samples DPriNxbP and DPTNxbP, between 55.1 and 56.8. Because of the structure and content of the hard segments is the same in each PUs, the soft segments affected the hydrogen bonding in hard segments and play key role on the hardness. The increased hardness of the PU sample based on PTMG (DPTNxbP) can be attributed to the even number of carbons, as the symmetric structure promotes segment ordering. Similarly, PU samples based on Priplast (DPriNxbP) exhibit increased hardness due to its semicrystalline nature, which facilitates partial ordering. Conversely, PU samples based on Velvetol (DVNxbP) demonstrate lower hardness as a result of its asymmetric polyol structure, which leads to lower molecular ordering. Results of hardness are in accordance to the calculated degree of phase separation, DPS (see Table 3).

Table 9
Density and swelling ratio of bio-based PUs.

Sample	Density [g/cm^3]	Swelling ratio (acetone) [%]	Swelling ratio (toluene) [%]
DPTNxbP	1.09±0.01	52.3±0.1	123.2±0.1
DPoNxbP	1.08±0.04	14.5±0.1	62.9±0.1
DVNxbP	1.09±0.02	70.3±0.1	135.7±0.1
DPriNxbP	1.05±0.01	81.9±0.1	166.5±0.1

3.9. Density and swelling

The chemical resistance of the samples to solvents was determined by a swelling test according to Eq. 4. The test was carried out using two solvents: polar (acetone) and non-polar (toluene). The results are presented in Table 9.

Conventional wisdom holds that interchain forces have a major influence on physico-mechanical properties (Bai et al., 2020). The test showed that the obtained materials do not degrade in the selected solvents. However, swelling of these materials has been observed as a result of exposure to such solvents. Presumably, this behavior of the samples is strongly influenced by the type of polyol, since the solvent enters the interstitial spaces. Therefore, a higher amount of solvent results in greater swelling. The swelling of the samples, rather than their decomposition, confirms their cross-linked structure. The degree of cross-linking determines the percentage of swelling of the sample and is affected by the structure of the materials, i.e. the presence of side groups on the chain. These materials can be described as solvent-resistant, as no surface modification was observed when tested.

The density of polyurethanes can be influenced by a number of factors, including chemical composition, molecular weight or potential cross-linking. However, the density of polyurethanes is reported in the literature to be in the range of 0.9–1.1 g/cm^3. In our work, the values of this property were found similar to these results and are in the typical range shown. Approximate density (1.09–1.16 g/cm^3) was reported by Silva et al. in their publication, where they developed bio-polyurethane coatings based on the same isocyanate – Desmodur eco N 7300 (Silva et al., 2023).

4. Conclusions

The use of naturally derived monomers is part of the sustainability movement, as it reduces dependence on petrochemical feedstocks and reduces environmental impact. Via application of modified bio-based isocyanate, it is possible to obtain highly transparent and soft bio-based polyurethane materials. The application of an isocyanate group modifier such as Cardolite NX-2026 provides a number of advantages of polyurethanes obtained with their use. Based on thermogravimetric studies and chemical resistance against organic solvents, an increase in thermal stability and chemical resistance was observed. Transparency of prepared polyurethanes is related to their highly amorphous structure which has been confirmed by DSC and XRD. DMA technique revealed that the bio-polyurethanes based on petrochemical polyols were characterized by good damping properties and higher stiffness at room temperature. In general, the obtained polyurethanes did not have sufficient tensile properties for many practical applications, but could still be used as a soft, transparent coating material. We demonstrated that swelling properties of bio-PU depend on their structure, as well as solvent polarity. To sum up, it is possible to obtain bio-based polyurethanes with the use of bio-based polyols, bioglycols and modified isocyanate trimer with satisfactory thermal characteristics. The use of bio-based monomers through solvent-free synthesis methods shows significant progress in the production of green polyurethanes with properties not inferior to those of classic polyurethanes and with the added benefit of high transparency. We are convinced that the promising properties of the obtained highly green polyurethanes can lead to many interesting applications, such as transparent and simultaneously soft products that do not require high mechanical strength, including transparent protective covers and protective films.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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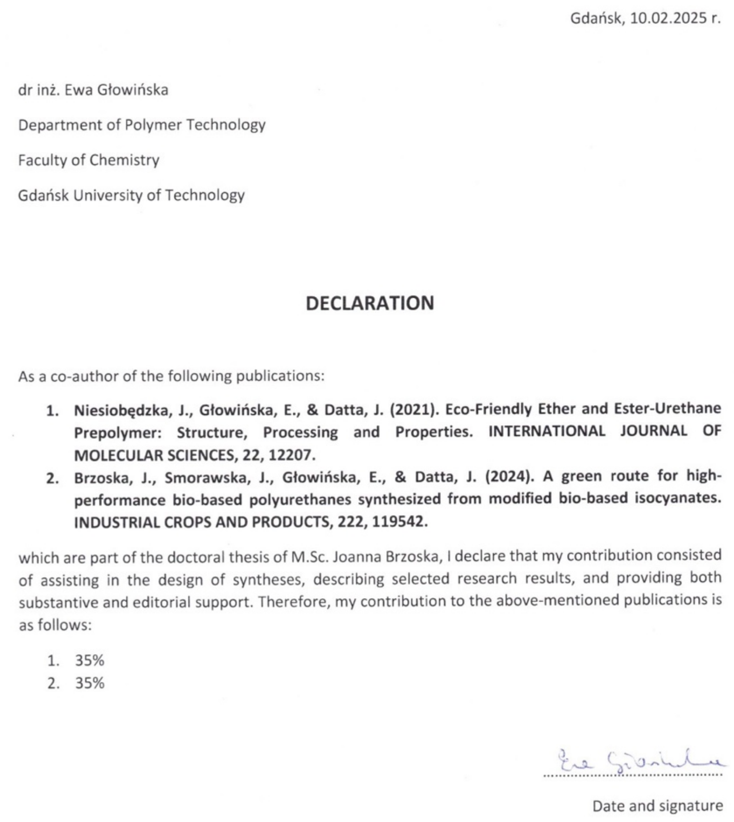
Co-authors’ statements of contribution:



Gdańsk, 10.02.2025 r.

dr inż. Ewa Głowińska

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DECLARATION

As a co-author of the following publications:

1. **Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.**
2. **Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.**

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of assisting in the design of syntheses, describing selected research results, and providing both substantive and editorial support. Therefore, my contribution to the above-mentioned publications is as follows:

1. 35%
2. 35%

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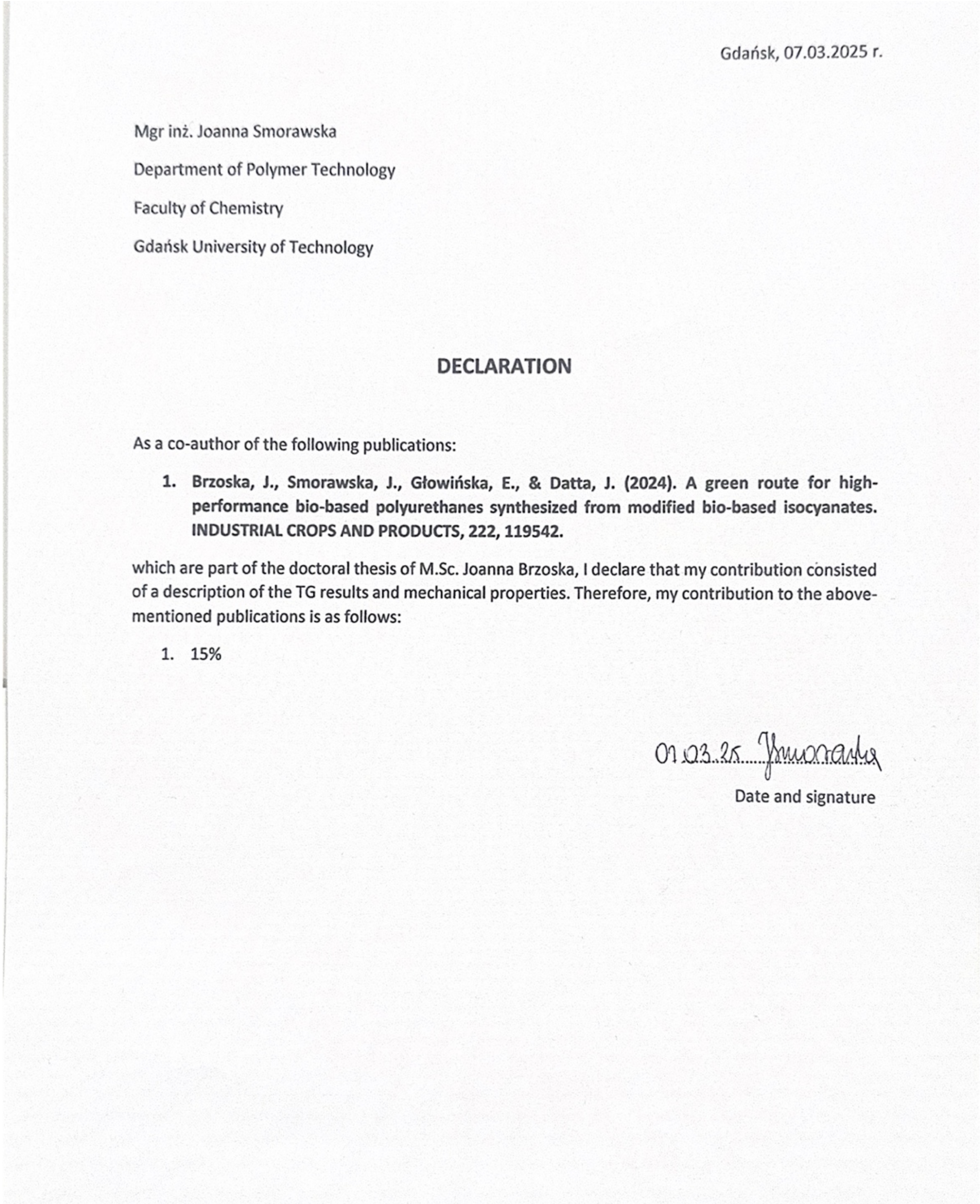
Date and signature



Gdańsk, 07.03.2025 r.

Mgr inż. Joanna Smorawska

Department of Polymer Technology

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DECLARATION

As a co-author of the following publications:

1. **Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.**

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of a description of the TG results and mechanical properties. Therefore, my contribution to the above-mentioned publications is as follows:

1. 15%

07.03.25 JSmorawska

Date and signature

Gdańsk, 07.03.2025 r.

Prof. dr hab. inż. Janusz Datta

Department of Polymer Technology

Faculty of Chemistry

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DECLARATION

As a co-author of the following publications:

1. Niesiobędzka, J., & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.

2. Niesiobędzka, J., Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.

3. Brzoska, J., Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.

4. Brzoska, J., Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.

which are part of the doctoral thesis of M.Sc. Joanna Brzoska, I declare that my contribution consisted of providing consultation during the execution of the experimental work, evaluating the literature review, and proofreading the papers. Therefore, my contribution to the above-mentioned publications is as follows:

1. 30%

2. 15%

3. 15%

4. 10%

……………………………………………

Date and signature

SECTION IV

SUMMARY

SUMMARY

Polyurethanes are versatile polymers with widespread applications in various industries, including automotive, construction and medical industries. Traditional methods of polyurethane synthesis typically rely on petroleum-based isocyanates such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). However, the environmental impact of these fossil-based materials and the toxicity of their synthesis intermediates, particularly phosgene, have raised significant concerns.

A promising alternative to traditional compounds is the use of bio-based equivalents. Bio-based isocyanates are derived from renewable resources such as plant oils, carbohydrates or lignocellulosic biomass. These sources provide a more environmentally friendly alternative while maintaining the desirable properties of traditional polyurethanes, such as flexibility, durability and abrasion resistance. In addition, the use of bio-based isocyanates reduces the carbon footprint of the production process, which is in line with the principles of green chemistry. An important process in the synthesis of bio-based isocyanates is the Curtius rearrangement. In this reaction, acyl azides are converted to isocyanates bypassing the need for phosgene. The Curtius rearrangement is particularly advantageous due to its relative simplicity and the potential to use bio-based starting materials. However, this synthesis has some drawbacks, namely the use of explosive azides, which makes obtaining larger quantities challenging.

Due to the extensive literature available on the synthesis of bio-based polyols and polyurethanes derived from them, this **thesis focuses on bio-based isocyanates and their application in polyurethane synthesis**, since this area still requires further development. Therefore, in this study, **various bio-based polyurethanes were synthesized using two commercially available bio-based isocyanates and two isocyanates synthesized specifically for this work by the Curtius rearrangement**.

A comprehensive approach to the application of bio-based isocyanates represents an undeniable novelty and challenge in this study. The thesis consisted of the following steps:

1. Synthesis of urethane prepolymers using the bio-based isocyanate Tolonate X FLO 100 and two different bio-based polyols (Priplast 3294 and Velvetol H2000).
2. Synthesis of polyurethanes from the prepolymers obtained in step 1 and a bio-based chain extender (Zemea PDO).
3. Characterization and study of the properties of the prepolymers and polyurethanes obtained in steps 1 and 2.
4. Modification of the commercial bio-based isocyanate Desmodur eco N 7300 to transform it into a difunctional isocyanate with increased green carbon content.
5. Use of the modified isocyanate from step 4 in the synthesis of polyurethanes with different polyols (both bio-based and petrochemical).
6. Investigation of the properties of the polyurethanes obtained in step 5.
7. Synthesis of BDI and bio-based ODI isocyanates via Curtius rearrangement using diphenylphosphoryl azide as a safer alternative to sodium azide.
8. Synthesis and characterization of polyurethanes based on BDI and ODI, together with bio-based polyols and a bio-based chain extender.

Various methods were used to characterize the obtained products. **Fourier Transform Infrared Spectroscopy (FTIR)** and **Nuclear Magnetic Resonance (NMR)** were employed to determine the structure of the monomers and products. **Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA)** and **Dynamic Mechanical Thermal Analysis (DMTA)** were used to investigate their thermal and thermomechanical properties. **Rheological measurements** provided information about the viscosity and behavior of the products and monomers. The crystalline structure of the products was determined using **Small and Wide-Angle X-ray Scattering (SWAXS)** or **X-ray Diffraction (XRD) techniques**.

As part of the thesis, materials characterized by green carbon contents ranging from 44 to 100% were obtained. The dissertation presented three different approaches to the use of bio-based isocyanates:

a. Use of the bio-isocyanate as supplied by the manufacturer (Tolonate X FLO 100);
b. Modification of the isocyanate by changing the isocyanate functionality and increasing the green carbon content of the final product (Desmodur Eco N7300);
c. Synthesis of an isocyanate by Curtius rearrangement (BDI and ODI).

All of the above isocyanates were successfully used in the synthesis of bio-based polyurethanes. The materials obtained had an increased green carbon content, making them an interesting alternative to commercially used polyurethanes, in line with the principles of sustainability. In addition, an isocyanate with 100% green carbon content was obtained by phosgene-free synthesis using the Curtius rearrangement.

All the polyaddition reactions carried out gave fully reacted polyurethanes, as confirmed by structural studies. The materials obtained were characterized by good thermal stability in the range of 237 ^{o}C to 299 ^{o}C. This stability is sufficient for most typical applications of polyurethane materials. However, their mechanical properties, such as tensile strength, were not competitive with their petrochemical counterparts. All the materials obtained showed similar degradation curves, mostly two or three step degradation, depending on the substrates used. The degradation curves observed were typical for polyurethanes. Depending on the substrate used, the polyurethanes were characterized by an amorphous or semi-crystalline structure. The amorphous structure was exhibited by samples based on a modified trifunctional isocyanate and on Tolonate X FLO 100. The rest of the samples were characterized by a semi-crystalline structure. All the obtained bio-based materials were totally or partially transparent.

The developed methods for the synthesis of bio-based polyurethanes provide a solid basis for future research into bio-based isocyanates. Although isocyanates have been known as raw materials for many years, good alternatives to their petrochemical counterparts remain unexplored. **The results presented in this thesis provide a comprehensive literature review of bio-based isocyanates, supplemented by newly obtained materials.**

The research represents a significant contribution to polyurethane chemistry and fills a gap in the use of bio-based isocyanates. It provides incontrovertible evidence that it is possible to obtain an isocyanate with 100% green carbon content using a phosgene-free method. This approach is innovative and in line with sustainability requirements.

However, the polyurethane industry still faces many challenges, such as improving the mechanical properties of bio-based polyurethanes. Nevertheless, it is important to note that as consumer awareness grows and the world evolves, the industry is also moving toward green alternatives to traditional polymer materials. Development in this direction is undeniably important and necessary. This thesis, based on 4 papers published in JCR-listed journals, will be an important contribution to the further development of the field.

SCIENTIFIC ACHIEVEMENTS

ORCID ID	0000-0003-4350-4527
Total Impact Factor	24,9
H-index	3
Citations (according to Scopus)	72
Participation in research projects	1
Papers published in JCR-listed journals	6
Papers published in non-JCR journals	1
Patent granted	1
Patent applications	2
Oral presentations at national and international conferences	2
Poster presentations at national and international conferences - presenting author	6
Poster presentations at national and international conferences - co-author	8

Papers published in JCR-listed journals:

1. **Brzoska, J.**, Datta, J., Konefał, R., Pokorny, V. & Benes, H. (2024). The influence of bio-based monomers on the structure and thermal properties of polyurethanes. SCIENTIFIC REPORTS, 14, 29042.
2. **Brzoska, J.**, Smorawska, J., Głowińska, E., & Datta, J. (2024). A green route for high-performance bio-based polyurethanes synthesized from modified bio-based isocyanates. INDUSTRIAL CROPS AND PRODUCTS, 222, 119542.
3. Głowińska, E., Smorawska, J., **Niesiobędzka, J**., Grocholska, J., & Datta, J. (2024). Synteza i charakterystyka „zielonych" mieszanin polimerowych na bazie biopochodnego termoplastycznego poliuretanu i octanomaślanu celulozy. Przemysł Chemiczny, 375-380.
4. Głowińska, E., Smorawska, J., **Niesiobędzka, J.**, & Datta, J. (2024). Structure versus hydrolytic and thermal stability of bio-based thermoplastic polyurethane elastomers composed of hard and soft building blocks with high content of green carbon. JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY, 149, 2147-2160.
5. **Niesiobędzka, J.**, & Datta, J. (2023). Challenges and recent advances in bio-based isocyanate production. GREEN CHEMISTRY, 25, 2482-2504.
6. **Niesiobędzka, J.**, Głowińska, E., & Datta, J. (2021). Eco-Friendly Ether and Ester-Urethane Prepolymer: Structure, Processing and Properties. INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES, 22, 12207.

Papers published in non-JCR journals:

1. Głowińska, E., **Niesiobędzka, J.**, Cybart, A., & Datta, J. (2020). Termoplastyczne elastomery poli(estro-uretanowe) otrzymywane z udziałem bio-glikolu poddane dwukrotnemu przetwórstwu. ELASTOMERY, 161-171.

Patent:

1. Janusz Datta, Paulina Parcheta, Izabela Zagożdżon, Joanna Niesiobędzka, „Sposób otrzymywania lanych poliuretanów o obniżonej palności”, Pat.245940.

Patent applications:

1. Paulina Parcheta-Szwindowska, Janusz Datta, Joanna Niesiobędzka, „Bio-poli(estro-etero)uretany i sposób ich otrzymywania”, application number: P.443832.
2. Joanna Niesiobędzka, Janusz Datta, Ewa Głowińska, Paulina Parcheta-Szwindowska, „Lany poliuretan o zwiększonej zawartości węgla pochodzenia biologicznego i sposób jego otrzymywania”, application number: P.446662.

Research internships:

1. Research traineeship organized by Netzsch (20.02 - 22.03.2023).
2. Research internship at the Institute of Macromolecular Chemistry Czech Academy of Sciences in Prague (1.09.2022-30.09.2022).

Participation in research projects:

1. WEAVE-UNISONO, project entitled “Sustainable polyurethanes "from the cradle to the grave" using enzymes” No. DEC - 2023/05/Y/ST8/00076.

Awards:

1. 1st place in the competition for the best poster at the "Przemysł Chemiczny" Conference organized by SITPChem in Warsaw.
2. Gold medal at The INTARG International Trade and Economic Innovation Fair 2022 for invention: „Sposób otrzymywania lanych

poliuretanów o obniżonej palności", authors: Janusz Datta, Paulina Parcheta-Szwindowska, Izabela Zagożdżon, Joanna Niesiobędzka, Patent application in the Polish Patent Office (PPO) with the number P.434425.

3. Special award from the World Invention Intellectual Property Associations for the invention: „Sposób otrzymywania lanych poliuretanów o obniżonej palności", authors: Janusz Datta, Paulina Parcheta-Szwindowska, Izabela Zagożdżon, Joanna Niesiobędzka, PATENT application at the Polish Patent Office (PPO) with patent number P.434425.).

Scholarships:

1. Minigrant Faculty of Chemistry (2021, 2022, 2023, 2024), Gdansk University of Technology.
2. 10.2023 – 09.2024 - Francium Supporting Outstanding Doctoral Candidates – scholarship of the IDUB program.
3. 10.2022 – 09.2023 - Francium Supporting Outstanding Doctoral Candidates – scholarship of the IDUB program.

Oral presentations at national and international conferences:

1. **Brzoska, J.**, Głowińska, E., Parcheta-Szwindowska, P. & Datta, J., *Prepolimery uretanowe otrzymywane z zastosowaniem bio-substratów – synteza i charakterystyka (Bio-based urethane prepolymers - Synthesis and characterisation)*, X Kongres Technologii Chemicznej, Politechnika Wrocławska, Wroclaw, Poland, 11-14 May 2022.
2. **Brzoska, J.** & Datta, J., *Effect of different bio-based raw materials on processing and thermal properties of urethane prepolymers*, XI International Scientific-Technical Conference „Advance in Petroleum and Gas Industry and Petrochemistry", The Department of Chemical Technology of Oil and Gas Processing, Lviv Polytechnic National

University, Lviv, Ukraine, 16 - 20 May 2022.

Poster presentations at national and international conferences - presenting author:

1. **Brzoska, J.**, Smorawska, J., Parcheta-Szwindowska, P., Głowińska, E. & Datta, J., *Bio-based polyisocyanate modification towards monomers for polyurethanes*, 15th Conference on Thermal Analysis and Calorimetry, PTKAT and Gdansk University of Technology, Zakopane, Poland, 8 – 12 September 2024.
2. **Brzoska, J.**, Głowińska, E. & Datta, J., *Synteza oraz właściwości poliuretanów otrzymywanych z wykorzystaniem biopochodnego modyfikatora (Synthesis and properties of polyurethanes prepared using a bio-based modifier)*, Przemysł Chemiczny, SITPChem, Warsaw, 5 – 7 December 2023.
3. **Brzoska, J.**, Głowińska, E., Parcheta-Szwindowska, P. & Datta, J., *Influence of bio-based isocyanates on the structure and properties of polyurethanes,* 8th International Seminar on Modern Polymeric Materials for Environmental Applications, Cracow University of Technology, Kraków, Poland, 17 – 19 May 2023.
4. **Brzoska, J.**, Głowińska, E., Parcheta-Szwindowska, P. & Datta, J., *Synthesis and characteristics of polyurethane foams obtained from bio-based monomers,* The Silesian Meetings on Polymer Materials POLYMAT 2022, CMPW PAN, Zabrze, Poland, 17 March 2022.
5. Głowińska, E., **Brzoska, J**., Machniak, M. & Datta, J., *Charakterystyka alifatycznych bio-poliuretanów otrzymywanych z wykorzystywaniem modyfikowanego epoksydowanego oleju sojowego (Characterization of aliphatic bio-polyurethanes obtained using modified epoxidized soybean oil),* X Kongres Technologii Chemicznej, Politechnika Wrocławska, Wroclaw, Poland, 11-14 May 2022.
6. **Brzoska, J.**, Głowińska, E., Parcheta-Szwindowska, P. & Datta, J.,

Pianki poliuretanowe otrzymywane z bio-prepolimerów etero-uretanowych – struktura i właściwości (Polyurethane foams obtained from bio-prepolymers of ether-urethane - structure and properties), 63. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, Polskie Towarzystwo Chemiczne, Lodz, Poland, 13 – 17 September 2021.

Poster presentations at national and international conferences - co-author:

1. Habaj, J., Parcheta-Szwindowska, P. **Brzoska, J.** & Datta J., *Synthesis and characterization of poly(ester-ether urethane)s obtained with the use of natural origin monomers*, XII International Scientific-Technical Conference "Advance in Petroleum and Gas Industry and Petrochemistry, The Department of Chemical Technology of Oil and Gas Processing, Lviv Polytechnic National University, Lviv, Ukraine, 20 - 24 May 2024.
2. Kopczyńska, K., Kordyzon, M., **Brzoska, J.**, Parcheta-Szwindowska, P. & Datta J., *Transparentne elastomery poliuretanowe - wpływ struktury chemicznej na charakterystykę termiczną materiałów (Transparent polyurethane elastomers - Influence of chemical structure on the thermal properties of materials),* Zastosowanie Sprzężonych Metod Analizy Termicznej w Badaniach Materiałów, NETZSH, Gdansk, Poland, 15 – 16 February 2023.
3. Kopczyńska, K., Parcheta-Szwindowska, P., Kordyzon, M., **Brzoska, J.** & Datta, J., *Bio-based polyester polyols for green polyurethane materials*, The Silesian Meetings on Polymer Materials POLYMAT 2022, CMPW PAN, Zabrze, Poland, 17 March 2022.
4. Głowińska, E., Machniak, M., Parcheta-Szwindowska, P., Włoch, M., **Brzoska, J**. & Datta, J., *Bio-polyurethanes obtained with the use of modified epoxidized soybean oil – synthesis and selected properties*, XI International Scientific-Technical Conference „Advance in Petroleum and Gas Industry and Petrochemistry", The Department of

Chemical Technology of Oil and Gas Processing, Lviv Polytechnic National University, Lviv, Ukraine, 16 - 20 May 2022.

5. Włoch, M., Datta, J., Głowińska, E. & **Brzoska, J**., *Glikolizat pianki poliuretanowej jako modyfikator właściwości mieszanek i wulkanizatów na bazie kauczuku naturalnego (Polyurethane foam glycolysate as a modifier of the properties of mixtures and vulcanizates based on natural rubber),* X Kongres Technologii Chemicznej, Politechnika Wrocławska, Wroclaw, Poland, 11-14 May 2022.
6. Czapiewski, M., Parcheta-Szwindowska, P., **Brzoska, J**., Głowińska, E. & Datta, J., *Bio-poliole poliestrowe otrzymywane z zastosowaniem mieszaniny bio-kwasów dikarboksylowych – synteza i charakterystyka (Polyester bio-polyols obtained with a mixture of bio-dicarboxylic acids - synthesis and characterization)*, 63. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, Polskie Towarzystwo Chemiczne, Lodz, Poland, 13 – 17 September 2021.
7. Głowińska, E., Parcheta-Szwindowska, P., **Brzoska, J**. & Datta, J., *Influence of the bio-based hard segments structure on the thermal, viscoelastic and mechanical properties of thermoplastic polyurethane elastomers*; 17th International Congress on Thermal Analysis Calorimetry, Polish Society of Calorimetry and Thermal Analysis, Krakow, Poland, 29 August – 2 September 2021.
8. Baranik, R., Kasprzyk, P., Koziński, P, Bagiński, F., Zagożdżon, I., **Brzoska, J.**, Parcheta-Szwindowska, P., Rohde, K., Głowińska, E., Włoch, M. & Datta, J., *Effect of different flame retardants on the thermal resistance and selective properties of the polyurethane elastomers*; X International Scientific-Technical Conference „Advance in Petroleum and Gas Industry and Petrochemistry", The Department of Chemical Technology of Oil and Gas Processing, Lviv Polytechnic National University, Ukraine, 18 - 23 May 2020.

Scientific research cooperation:

1. Institute of Macromolecular Chemistry, Polymer Materials and Technologies, Czech Academy of Sciences, Prague, Czech Republic
2. Department of Inorganic Chemistry at Gdansk University of Technology, Gdansk, Poland
3. Department of Organic Chemistry at Gdansk University of Technology, Gdansk, Poland

Activities to promote science:

1. Co-organizer of science and technology shows as part of the Baltic Science Festival in 2021–2024.
2. Participation in the organization of the 15th Conference on Thermal Analysis and Calorimetry (2024) in Zakopane.
3. Participation in the organization of the conference „Zastosowanie sprzężonych metod analizy termicznej w badaniach materiałów” (2023) in Gdansk.
4. Member of the scientific club "TechPol”.
5. Participation in Gdansk Tech open days and during high school visits at the department.
6. Representative of GUT at the scientific stand as part of the 'Zdolni z Pomorza' project.
7. Member of the Doctoral Students' Self-government for the 2020/2021 term.