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Sustainable polyurethanes: toward new cutting-edge opportunities



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ABSTRACT

Polyurethanes (PU) are ranked amongst the 6th most manufactured worldwide polymers and are widely used in a variety of applications due to the diversity of properties they offer. Nevertheless, PUs are raising questions around environmental, legislative, health, and recycling concerns. In this context, due to the high isocyanate toxicity, blocked isocyanates, waterborne PU systems, and non-isocyanate polyurethane (NIPU) were introduced to prevent isocyanate handling risks. Moreover, sustainable feedstocks stood out to synthesize greener PU. In particular, bio-based polyfunctional short alcohol and isocyanate compounds have emerged to design fully bio-based PU materials with targeted chemical and mechanical properties. Finally, the large amounts of PU that have been placed on the market are now leading to environmental issues regarding its accumulation in the environment. Several methods have thus been recently developed to facilitate their end-of-life management and recyclability.

This review provides a complete overview on the most recent advances on PUs synthesis with focus on the replacement of toxic isocyanates and petroleum-based resources, the use of greener processes, and their recycling methods. After a quick summary on PUs history and worldwide situation, different bio-based alcohols and isocyanates introduced on academic and industrial sides, and the corresponding PU are outlined. Furthermore, different synthesis pathways to produce NIPUs are discussed. Finally, the enzymatic and chemical recycling of PUs are outlined.

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List of abbreviations: 5CC, 5-membered cyclo-carbonate; BA, Blowing agent; BACC, Aromatic-based cyclic carbonate; BDO, 1,4-butane diol; BMC-C6, Hexamethylene dicarbamate; BO, Butylene oxide; Boc₂O, Di-*ter*-butyl dicarbonate; CA, Carbamate / aldehyde; CAN, Covalent adaptable network; CC, Cyclic carbonate; CLIP, Continuous liquid interface production technology; CMR, Carcinogenic mutagenic or reprotoxic; CNSL, Cashew nutshell liquid; CYCC, Aliphatic cyclic carbonates; DABCO, 1,4-diazabicyclo[2.2.2]octane; DBTDL, Dibutyltin dilaurate; DEG, diethylene glycol; DETA, Diethylene triamine; DLP, Digital light processing; DMAP, 4-dimethylaminopyridine; DMC, Dimethyl carbonate; DSC, Differential scanning calorimetry; EA, Ethanol amine; EG, Ethylene glycol; EO, Ethylene oxide; FDM, Fused deposition modeling; FTIR, Fourier-transform infrared spectroscopy; GMO, Genetically modified organism; GWP, Global warming potential; HDI, Hexamethylene diisocyanate; HEMA, 2-hydroxyethyl methacrylate; HEW, Hydroxyl equivalent weight; HFC, Hydrofluorocarbons; HFO, Hydrofluoro-olefin; HMDI, Hydrogenated methylene diphenyl diisocyanate; HS, Hard segment; IEV, Isocyanate equivalent weight; IPDA, Isophorone diamine; IPDI, Isophorone diisocyanate; LCA, Life cycle analysis; LDI, Lysine ethyl-ester diisocyanate; LFDm, Liquid-frozen deposition manufacturing; LPUe, Lignin based polyurethane elastomer; MALDI-TOF, Matrix assisted laser desorption ionization-time of flight; MDA, 4,4'-methylenedianiline; MDI, Diphenylmethane diisocyanate; MPDO, 2-methyl-1,3 propanediol; NIPU, Non-isocyanate polyurethane; NIPUA, Non-isocyanate polyurethane acrylate; NMR, Nuclear magnetic resonance; PBT, Polybutylene terephthalate; PDI, Pentamethylene diisocyanate; PDO, 1,3-propanediol; PE, Polyethylene; PEA, Polyether amine; PEG, Polyethylene glycol; PET, Polyethylene terephthalate; PHA, Polyhydroxyalkanoate; PHU, Polyhydroxyurethane; PHUA, poly(hydroxyurethane-acrylate); PLA, Poly(lactic acid); PO, Propylene oxide; PO3G, Biobased polypropanediol from Weylchem - Velvetol ®; PP, Polypropylene; PPG, Polypropylene glycol; PPO, Poly(propylene oxide); PTMO, Poly(tetramethylene oxide); PTT, Polytrimethylene terephthalate; PU, Polyurethane; PUA, Polyurethane acrylate; PUF, Polyurethane foam; PδDL, Poly(δ-decalactone); REACH, Registration evaluation authorization and restriction of chemicals; REX, Reactive extrusion; RIM, Reaction injection moulding; ROP, Ring-opening polymerization; SEM, Scattering electron microscopy; SLA, Stereolithography; SLS, Selective laser sintering; SS, Soft segment; TBAB, Tetrabutylammonium bromide; TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene; T_c, Crystallization temperature; TDA, 2,4-Toluylene diamine; TDI, Toluene diisocyanate; TETA, Triethylenetetramine; T_g, Glass transition temperature; TGA, Thermogravimetric analysis; THF, Tetrahydrofuran; T_m, Melting temperature; TMPTC, Trimethylol propane triscarbonate; TPU, Thermoplastic polyurethane; VOC, Volatile organic compounds; WPU, Waterborne polyurethane.

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E-mail addresses: julien.pinaud@umontpellier.fr (J. Pinaud), sylvain.caillol@enscm.fr (S. Caillol).<https://doi.org/10.1016/j.progpolymsci.2024.101805>0079-6700/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>)

1. Introduction

Polyurethanes (PUs) are a family of commodity polymers representing a significant part of the polymer market. They are present in many products such as furniture, coatings, adhesives, constructional materials, paints, elastomers, and synthetic skin among many others [1]. Discovered by Otto Bayer in 1937 [2], the polyurethane demand has not stop growing during the second half of the 20th century and is expected to continue growing for the next few years. In fact, it is currently one of the most common, versatile and researched material in the world. Specifically, the PU global market size was priced at \$72.82 billion in 2021 and is projected to increase during the next years with a compound annual growth rate (CAGR) of 4.3 % from 2022 to 2030 [3]. The PU market is usually segmented in five uneven parts including foams (65% of the market), coatings (13%), elastomers (12%), adhesives (7%) and the biomedical field (3%), as displayed in Fig. 1 [1,4].

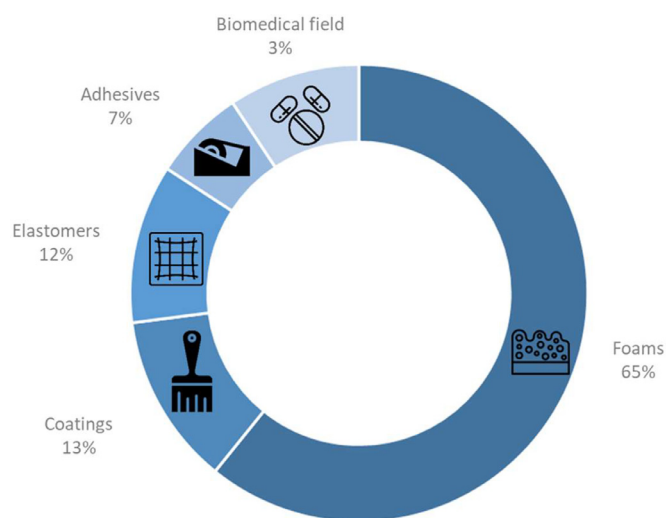
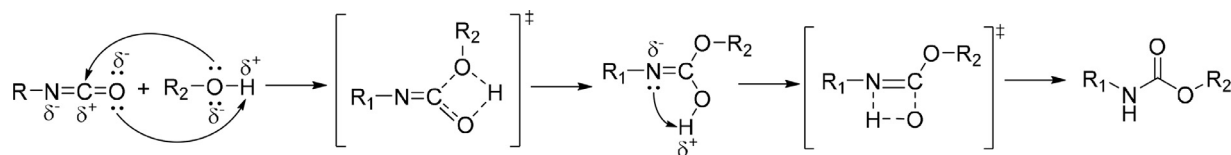


Fig. 1. PU market in 2022 by applications.



Scheme 1. Reaction mechanism of an isocyanate and an alcohol.

This success does not only come from the good thermal and mechanical properties of polyurethanes, but also from the large range of commercially available PU building blocks that allow bringing specific properties to the final material such as flexibility, rigidity, lightness, abrasion resistance or biodegradability among others. Moreover, the reaction of isocyanates with multifunctional alcohol compounds, also called polyols, leading to PU materials (Scheme 1) displays fast kinetics at room temperature in the presence of catalysts, thus allowing for rapid cure and fast processing in the PU industry. All these advantages make PU very attractive, resulting in a global market by volume of PU representing today 25 million metric tons that is expected to grow up to 31 million metric tons by 2030 [5].

Nevertheless, despite all their advantages, PU face both environmental and health issues that have been the focus of intense research over the past ten years. Regarding environmental aspects, PU raise concerns both during their manufacturing and at the end of their life. Indeed, most PU are petroleum-based materials

that end-up their life cycle either as energy source in incinerators, which contributes to global warming through carbon dioxide (CO₂) emissions or buried in landfills (representing about 50 % of PU wastes), which gives rise to soil and ecosystems pollution [6,7]. Regarding health concerns, apart from alcohol monomers, most chemicals employed to synthesize PU such as isocyanates or dibutyltin dilaurate (DBTDL), one of the most employed catalysts for the isocyanate/alcohol reaction, are substances considered toxic at low concentration or by inhalation, and sometimes carcinogenic, mutagenic or reprotoxic (CMR) [8–10]. Moreover, isocyanates are industrially synthesized from extremely toxic and harmful reagents such as phosgene, a gas that causes lungs irritation and eventually death when inhaled at concentration above 4 ppm [11,12]. To limit the carbon footprint and eco-toxicity of PU, a large range of renewable building blocks (both diols/polyols and isocyanates) have thus been introduced on the market. Additionally, both chemical and mechanical recycling of PU have been developed, as recently reviewed by Polo Fonseca *et al.* [13]. Going further, synthesizing or shaping PU using green processes, *i.e.* energy efficient processes or processes that comply with atom economy by limiting or suppressing PU material wastes or volatile organic compounds (VOC), is also the subject of a growing interest both at academic or industrial levels [14]. Besides, non-isocyanate polyurethane (NIPU) and organic catalysts were found beneficial to limit toxicity associated with PU synthesis. Therefore, the present review intends to provide a comprehensive overview of the various strategies that have been developed both at academic and industrial levels to increase PU sustainability over their entire life cycle (Scheme 2) as well as to limit the toxicity of starting building blocks. After a summary on PU chemistry, the first two parts of this review are devoted to the different bio-based reagents that can be used to prepare bio-based or partially bio-based PUs [15–19]. While the third part aims to cover the isocyanate-free synthetic pathways to PU [19–24], the fourth part is dedicated to the green processes that can be employed to provide the desired shape to PU. Finally, PUs are examined in the context of circular economy and end-of-life management [25–27].

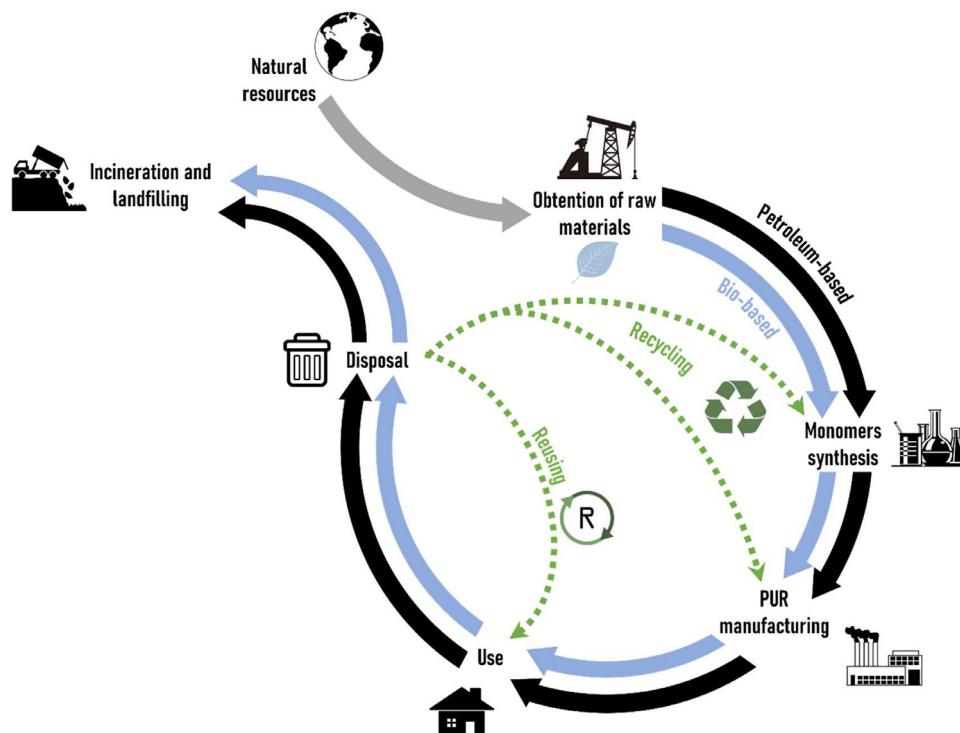
2. PU from basics

2.1. PU chemistry and synthesis

PUs are obtained by addition step-growth polymerization between a polyfunctional alcohol and a polyfunctional isocyanate producing carbamate groups, commonly called urethane groups. This reaction leads to linear or crosslinked materials, depending on the average functionality of monomers.

PUs are generally synthesized in the presence of a basic or an acidic catalyst, which will either activate the alcohol function or the isocyanate function [28]. Catalyst activation modes during urethane formation will be discussed in part 6.4.

The reactivity between an alcohol and an isocyanate is closely related to the nature of the compounds. Isocyanates compounds can have an aliphatic, a cycloaliphatic or an aromatic structure and therefore, display different reactivity. Due to the delocalization of the negative charge in the aromatic ring, as seen in Scheme 3,



Scheme 2. General scheme of PU life cycle.



Scheme 3. Electron delocalization on an aromatic isocyanate.

aromatic isocyanate compounds are more reactive than aliphatic or cycloaliphatic counterparts. In an aromatic system, the negative charge is delocalized into the π electron ring system. Consequently, the partial positive charge on the carbon atom carried by the isocyanate group will increase and the final reactivity of the compound will rise (more electrophilic) [29].

Other substituents on the aromatic ring also affect the reactivity of the isocyanate: electron withdrawing groups in ortho or para position increase the reactivity, whereas electron donating groups lower the reactivity of the isocyanate function. For these reasons, aliphatic or cycloaliphatic isocyanates are less reactive than aromatic ones. Regarding cycloaliphatic or aliphatic isocyanate structures, different effects can have an influence on their reactivity like inductive effect of side groups or steric hindrance, making reactivity classification of isocyanate compounds difficult.

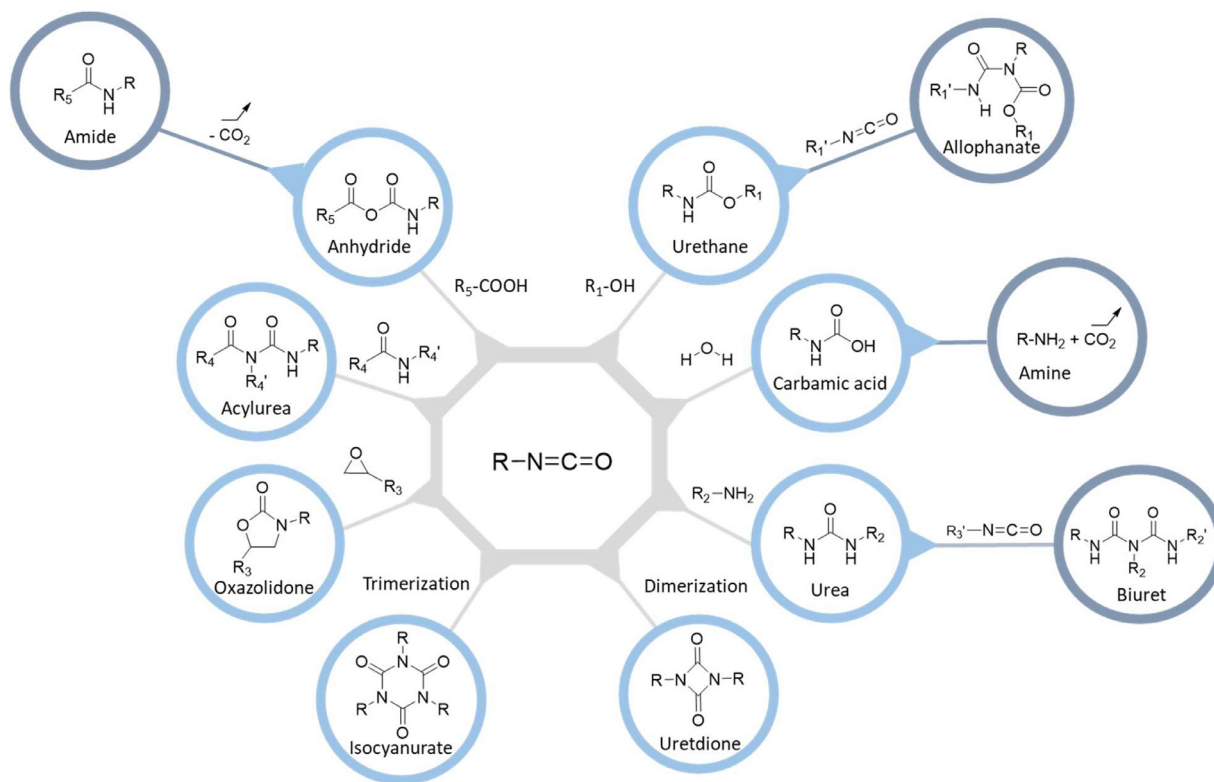
Since isocyanates are electrophiles, they react with nucleophiles such as alcohols, amines and water. Amines being stronger nucleophiles than alcohol or water, they are the most reactive with isocyanates (the relative reaction rate constants of these nucleophiles

with phenyl isocyanate are reported in Table 1) and lead to an almost instantaneous reaction to provide urea bonds. As such, when amines are present in the starting formulation, resulting materials are often called polyurethane-urea [30]. Due to their high reactivity with isocyanates, amines have often been employed to prepare waterborne polyurethane dispersions as explained in Section 6.2. Besides, amines can also be employed to introduce urea groups into "polyurethanes" to form a hard segments as described in the next section. Nevertheless, polyols remain the most employed starting compound to prepare polyurethanes. However, it should be noted that most polyurethanes prepared solely from polyols, are materials that actually display both carbamate and urea groups in their structure. Indeed, water is often present (sometimes as traces) in alcohol compounds due to hydrogen bonding and can thus react with isocyanates to form amines through the carbamic acid intermediate (Scheme 4). The reactivity order of nucleophiles, when no catalyst is used, increases as follows: phenols, tertiary alcohols, secondary alcohols, water, primary alcohols and amines [31].

Table 1

Kinetic rate constants and activation energies of the reaction of phenyl isocyanate (in toluene at 99%) with a few hydrogen donors [31].

Hydrogen donor	Rate constant ($10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	Activation energy ($\text{kcal}\cdot\text{mol}^{-1}$)
Aromatic amine	10-20	-
Primary OH	2-4	8-9
Secondary OH	1	10
Water	0.4	11
Tertiary OH	0.01	-
Phenol	0.01	-



Scheme 4. Key reactions involving isocyanates [33], Copyright 2023. Adapted with permission from Taylor & Francis eBooks.

Isocyanates are versatile and highly reactive compounds that can react with numerous chemical products, including themselves. Chemists in the PU industry have largely taken advantage from this reactivity to diversify the chemical structure of resulting PU and thus to obtain PU with specific properties. In particular, the trimerization of isocyanates to form isocyanurates has proven very beneficial for the production of isocyanates with a functionality greater than 2 and for imparting rigidity and thermal stability in PU materials [32]. A summary of the main reactions involving isocyanates is depicted in Scheme 4.

Only the reaction between alcohols and isocyanates gives rise to urethane groups. In the following paragraphs, diol compounds, which have a functionality equal to 2, will be distinguished from polyfunctional alcohols (polyol), with a functionality strictly higher than 2. Similarly, diisocyanates will be employed for chemicals with NCO functionality of 2, while polyisocyanates will refer to molecules or macromolecules with an NCO functionality strictly over 2.

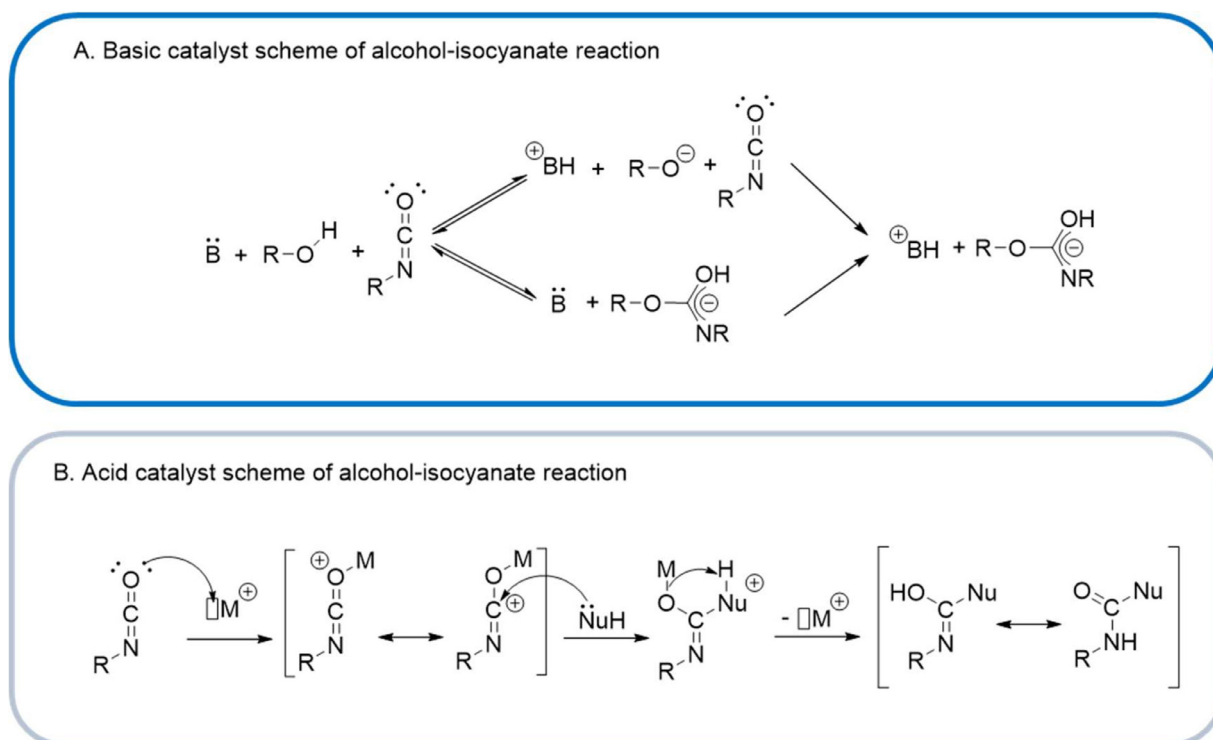
Despite the reaction between an alcohol and an isocyanate can be performed at moderate temperature (80°C - 100°C) in few hours, using a catalyst to allow the reaction to take place at room temperature has been the preferred strategy for PU synthesis at industrial level. Indeed, catalysts play a key role in controlling the reaction kinetics, reducing curing temperatures and durations, thus saving energy and processing times [34]. The isocyanate-alcohol reaction can be catalyzed either by basic catalysts or acid catalysts. Basic catalysts (Scheme 5-A) activate the alcohol function by interacting with the H atom, thus increasing electron density and nucleophilicity of the O atom. Acid catalysts (Scheme 5-B) activate the isocyanate function by pulling electrons of the O atom, eventually bonding. It results in a decrease of the electron density at the carbon of the isocyanate that enhances the nucleophilic attack by the alcohol.

Basically, conventional catalysts can be classified into two main categories: metal-based salt catalysts, which act as Lewis acids

[35], and hindered amine catalysts, which act as Lewis bases. According to their mode of activation, Lewis Acids promote the isocyanate-alcohol reaction over the isocyanate-water reaction, while basic catalysts behave antagonistically. Depending on the final application of the PU material (TPU, thermoset or foam), the choice of the catalyst is crucial.

2.2. TPU vs PU thermosets

PU structures can be divided into two main groups: thermosets and thermoplastics polyurethanes (TPUs). TPUs consist of a linear or branched structure obtained from the reaction between diols, and eventually diamines, and diisocyanates or a mixture of polyol and polyisocyanates with an average functionality ≤ 2.1 . TPUs exhibit tunable flexibility, mechanical strength, good abrasion resistance and elasticity [36–38]. Since TPUs are composed of polymeric chains that are maintained together only by weak intermolecular forces (as opposed to PU thermosets where polymer chains are linked together by covalent bonds), they are fully recyclable and reprocessable materials [39,40]. Depending on the type of polyol employed to synthesize them, TPUs can vary from soft elastomers to hard plastics. Their microstructure displays several phases arising from the micro-segregation between hard segments (HS) and soft segments (SS). This segregation is due to physical interactions between PU chains through hydrogen-bonding between urethane/urea functions and the different polarities and the chemical nature of blocks. HS act as physical crosslinking and are associated into domains because of the rigidity and hydrogen bonding of the urethane/urea bonds [41]. SS mainly consist of the long polyol backbone (polyester, polyether and polycarbonate). Indeed, HS and SS are thermodynamically incompatible leading to a TPU with HS and SS separated into microphases or domains [42]. When the material is heated above the melting temperature of the HS, it leads to a homogenous viscous melt that can be processed by different techniques such as injection molding, extrusion, blow mold-



Scheme 5. Reactional scheme of isocyanate-alcohol catalysis.

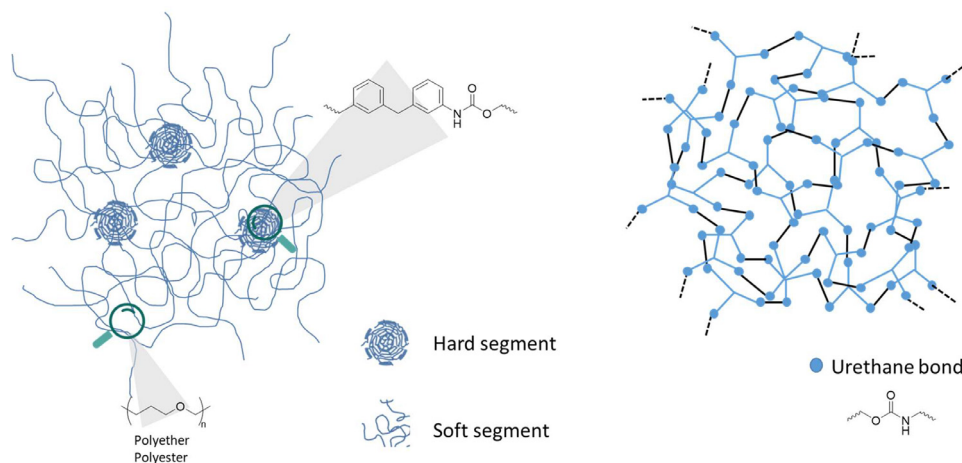


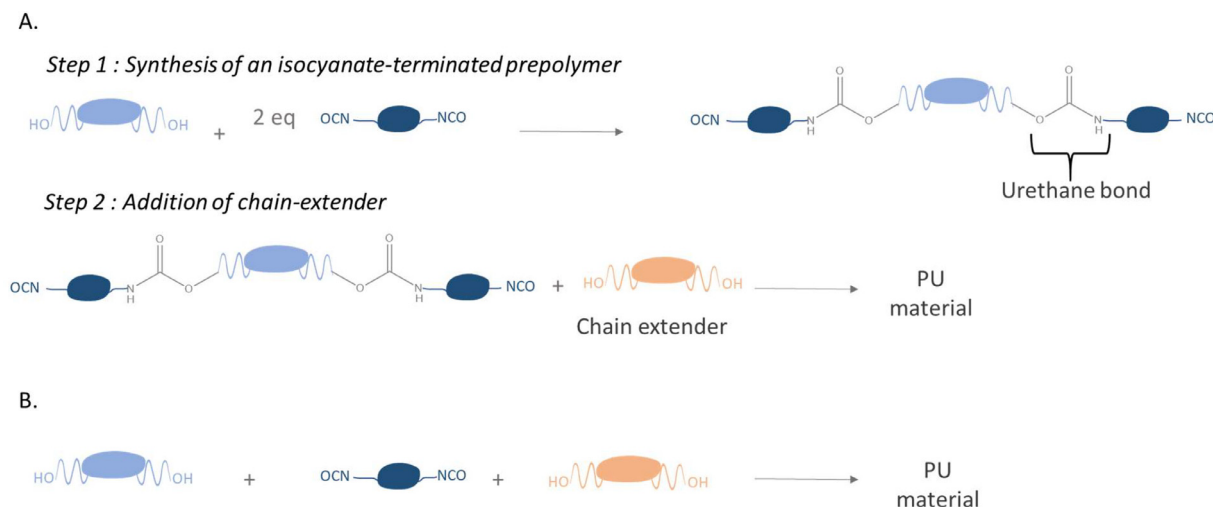
Fig. 2. Schematic representation of thermoplastic (left) vs thermoset (right) PU materials. In this representation, the thermoset material is composed of trifunctional and difunctional monomers. Chemical and polymer structures illustrated are taken as an example.

ing, compression molding or solution coating [38]. Consequently, TPU can be reshaped multiple times without altering their physical properties.

In contrast to TPUs, thermoset PUs are chemically crosslinked 3D-networks containing covalent bonds, as illustrated in Fig. 2. Thermoset PU materials are obtained through a curing process that can be induced either by heat, radiation or using suitable catalysts. The use of formulations composed of multifunctional monomers with an average functionality > 2.1 is necessary to obtain a 3D network with cross-linking nodes [43]. Therefore, thermosets cannot be thermo-reprocessed, reshaped and are insoluble and infusible. However, they exhibit higher thermic, mechanical, chemical, hydrolysis, and abrasive resistances. Thermoset PU are usually prepared by two synthetic routes: the two-step method and the one pot technique, as seen in Scheme 6 [36].

The one pot process consists of directly mixing polyols and polyisocyanates, eventually in the presence of additives (catalysts, blowing agent...). Because of its simplicity, it is commonly employed in industry, either to produce TPUs or thermosets. However, in the latter case, the starting components are directly injected into the mold that provides the shape of the final product and that acts as reaction vessel. The key parameter in the one pot synthesis is the high reactivity of the isocyanate group ($-NCO$) towards labile hydrogen from alcohols.

In the two-step method, a prepolymer with $-NCO$ chain-ends is first synthesized by reaction of a long diol such as a polyester or a polyether, with an excess of diisocyanate. The reaction is carried out until all hydroxyl groups are reacted. Secondly, a chain extender, usually a short diol such as 1,4-butanediol (BDO) or a polyol such as glycerol, is added to react with the prepolymer, leading to



Scheme 6. Synthesis of PU material through two-steps (A) and one pot (B) method.

long TPU chains with soft and hard segments or to a thermoset polyurethane. A polyfunctional chain extender must be used to design thermoset materials when a difunctional prepolymer is designed while a difunctional chain extender will be used for thermoplastic materials. This method allows a fine control of the final PU structure and leads to high molar mass TPU (for example \bar{M}_n easily reach $100,000 \text{ g}\cdot\text{mol}^{-1}$) [44].

To ensure a rigorous stoichiometry between isocyanate and alcohol, different methods have been standardized, allowing a convenient way to calculate and control hydroxyl and isocyanate content. Among them, the most used in industry is the calculation of NCO percentage (%NCO). It is determined by back-titration of NCO functions through ISO 14896 standard. First, Isocyanates groups are reacted with an excess of amine. The non-reacted amines are then titrated with a solution of hydrochloric acid. Similarly, the hydroxyl value of diols or polyols can be determined by back-titration of alcohol functions (-OH) through ISO 14900 or ASTM D4274. In this case, hydroxyl groups are acetylated in a solution of acetic anhydride in pyridine catalyzed by imidazole (the excess reagent is hydrolyzed with water). The resulting acetic acid is then titrated with sodium hydroxide solution.

To facilitate the determination of relative amounts of isocyanate/alcohols to be employed, the hydroxyl equivalent weight (HEW) and isocyanate equivalent weight (IEW) have been introduced. They represent the mass of compound that contains one mole of alcohol or isocyanate function. The equivalent weight can also be defined as the weight of a compound per reactive site: $\text{EW} = \frac{\text{MW}}{f}$. The HEW or IEW are usually determined by titration using various analytical techniques such ^1H nuclear magnetic resonance (NMR) determination, with an internal standard (usually benzophenone or trioxane) by the integration of the signals corresponding to the hydrogen that are adjacent to the hydroxyl/isocyanate moiety. It is then calculated as follows:

$$\text{HEW} = \frac{m_{\text{alcohol}} \times N_{\text{H eq alcohol}} \times \int_{7.28}^{7.87} \text{benzophenone}}{m_{\text{benzophenone}} \times N_{\text{H eq benzophenone}} \times \int_x^x \text{alcohol}}$$

Equation 1. Equation to determine the HEW of a polyol where m_{alcohol} and $m_{\text{benzophenone}}$ are the introduced masses of alcohol and benzophenone, $N_{\text{H eq alcohol}}$ is the number of equivalent hydrogens next to the hydroxyl moiety, $N_{\text{H eq benzophenone}}$ is the number of hydrogens on the aromatic ring of benzophenone.

Finally, it is possible to calculate the equivalent weight of a compound from its OH value in the case of polyols or its NCO per-

centage in the case of polyisocyanates.

$$\text{HEW} = \frac{56,1 \times 1000}{\text{OH value}} \text{ g/eq} \quad \text{IEW} = \frac{42,02 \times 100}{\text{NCO}} \text{ g/eq}$$

Another method to calculate the HEW by NMR, particularly useful when signals of the hydrogen overlap with other signals, is the phosphitylation method [45,46]. In this method, an excess of 4,4'-trimethylenedipiperidine is reacted with the hydroxyl groups (including the ones from COOH functions), in the presence of pyridine. It leads to a phosphitylated compound, which signals can be easily identified in RMN ^{13}P .

2.3. PU foams

PU foams (PUFs) are thermoset PU wherein, in addition to polyols and polyisocyanates, a variety of chemicals such as blowing agents (BAs), catalyst or surfactant are involved. PUFs are divided in two main families, according to their rigidities: soft foams and hard foams [47]. Soft foams are mainly used as cushioning material in transportation, furniture, bedding, carpet underlay and packaging. Rigid foams are primarily used as insulation material in construction and refrigeration applications.

There are two main types of BAs: physical blowing agents and chemical blowing agents [48–50]. Physical BAs will expand the cellular structure of the polymer by vaporization induced by the reaction exotherm. The most common used physical BAs are components with low boiling point such as cyclopentane, hydrofluorocarbons (HFC), hydrofluoroolefin (HFO), isobutane, dimethyl ether (DME) and propane. Physical BAs can also be gases that are directly injected during the curing of the material such as butane or carbon dioxide.

Historically, the use of CFCs (1st generation of F-gas) and later HCFCs (2nd generation of F-gas) as physical blowing agents for closed cell PUFs was very widespread, especially in insulation foams since they provide excellent insulation properties for the rigid polyurethane foams compared to other blowing agents. Additionally, they are easily handled liquefied gases molecules that remain in the PUF to maintain the foam's thermal insulation properties. However, CFCs are very stable molecules that, once released in the atmosphere, can reach the stratosphere and destroy ozone, as alerted by Rowland and Molina [51]. As a consequence, after extensive scientific, social and political controversy, drastic reductions in the production of CFCs were ratified in 1987 with the Montreal Protocol [52]. On the other hand, HCFCs containing carbon-hydrogen bonds, they are less stable than CFCs and there-

Table 2
Common HFCs and HFO used as blowing agent in polyurethane rigid foam [56].

Compound	Carbon dioxide	1,1,1,3,3-pentafluoropropane	1,1,1,3,3-pentafluorobutane	1,1,1,2,3,3,3-heptafluoropropane	1-Chloro-3,3,3-trifluoropropene
Commercial name	-	HFC-245fa	HFC-365mfc	HFC-227ea	HFO-1233zd
Chemical formula	CO ₂	C ₃ H ₃ F ₅	C ₄ H ₅ F ₅	C ₃ HF ₇	C ₃ H ₂ F ₃ Cl
Boiling point (°C)	-78.5	15.3	40.2	-16.5	19.0
Vapor thermal conductivity at 25°C (mW·m ⁻¹ ·K ⁻¹)	16.3	12.2	10.6	13.3	10.5

fore less destructive to ozone. Nevertheless, they still have a significant impact on the ozone layer and are powerful greenhouse gases [53]. Accordingly, action have been taken with the Copenhagen Amendment, signed in 1992, that calls for the ban of HCFCs by 2030 for industrialized countries and by 2040 for developing countries [54]. Of note, the use of HCFCs in the European Union is banned since 1st January 2010 [55].

Currently, HFCs (3rd generation of F-gas) and HFOs (4th generation of F-gas) are widely used as BAs for rigid PUF for building insulation. The most common gases used in the production of polyurethane rigid foam are displayed in Table 2.

On the other side, chemical BAs are added to the polymer either prior to the polymerization or during the polymerization. Chemical BAs are compounds that release gas through a thermal decomposition or a chemical reaction [48,57]. Among them, water is certainly the most employed since it is largely available, cheap and reacts efficiently with isocyanates to form carbon dioxide as explained in Section 2.1. As released carbon dioxide thus contributes to the expansion of the polymer matrix and subsequently to the formation of an open cell foam.

3. Bio-based polyols: news options for polyurethane industries

As explained before, polyols are valuable products used as reagents to design polyurethanes. Polyols can be obtained from renewable resources as an alternative to petrochemical-based raw materials. In this part, both commercial and academically designed bio-based polyols are presented, and the properties of the resulting polymers will be discussed. Bio-based polyols can be sorted into two main categories: molecular bio-based polyols and macromolecular bio-based polyols.

3.1. Molecular bio-based diols/polyols

3.1.1. Short bio-based diols/polyols

Short molecules have a better reactivity than long-chain alkyl molecules. Indeed, hydroxyl functions on short molecules are less hindered and have a better mobility. Therefore, short molecules are used as chain extenders to complete polymer materials formation or to design linear polymers such as polyester polyols.

The most used short diols from petrochemical resource are ethylene glycol (EG), diethylene glycol (DEG), 1,3-propanediol (PDO), 2-methyl-1,3-propanediol (MPDO) and 1,4-butanediol (BDO) among others (Fig. 3). These low-cost molecules provide materials with good hardness values, abrasion resistance and hydrolytic stability [58].

Chemical companies successfully synthesized some compounds mentioned above in a bio-based version, without altering the final properties of the PU. The main target in synthesizing bio-based versions of short polyols that already exist is to propose more sustainable and environmentally friendly PU, with the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and processes. Since short polyols are one of the main components in the preparation of PU adhesives or TPU, they can be easily replaced by bio-based alternatives. If bio-based alternatives are, in all respects, identical to the petrochemical molecule (chemical structure, aspect, reactivity), they can be used without changing the starting formulations and even the established process. Consequently, the properties of resulting PUs should not be changed.

Different synthesis routes, eliminating the need of fossil fuel-based feedstocks, are available to access bio-based BDO from sugars or cellulosic feedstocks. As explained in Scheme 7, the concerned technologies can take a direct pathway (fermentation of sugars) or an indirect pathway that involves the bio-based intermediate succinic acid [59].

Genomatica company and formerly BioAmber (went bankrupt in 2018) have adopted two synthetic pathways to obtain bio-BDO which are completely different. One requires the use of a chemical catalyst and the other one is driven by microbial fermentation. BioAmber produced bio-BDO by hydrogenation of succinic acid through a single catalytic process [60], whereas Genomatica has developed a bio-BDO production through the fermentation process of crop-derived sugars [61], demonstrating that bio-engineering techniques can be a valuable and viable alternative to chemical synthesis that involves toxic solvent and petrochemical-based catalysts.

Regarding PDO, Metex Noovista launched a product known as TILAMAR® PDO that is mainly used as a personal care ingredient. The resulting PDO, produced by fermentation process, is 100% bio-based, from non-genetically modified organism (GMO), and palm-oil free. DuPont Tate & Lyle Bio Products also produce bio-based PDO, named Susterra®, via fermentation of corn sugar [62]. In both cases, bio-PDO is produced by fermentation methods and promotes the use of renewable raw materials.

Among the most employed short bio-based polyols, glycerol, also known as glycerin, is the most abundant [63]. It can be obtained as a by-product from saponification and hydrolysis reactions in oleochemical plants or from transesterification reaction during biodiesel production [64,65]. There are many glycerol suppliers worldwide such Cargill, Perstorp, Archer Daniels Midland Co,

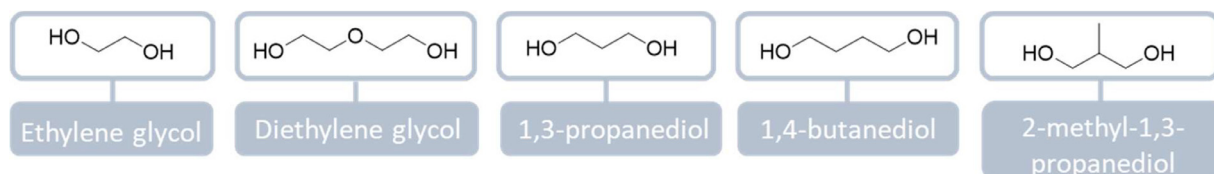
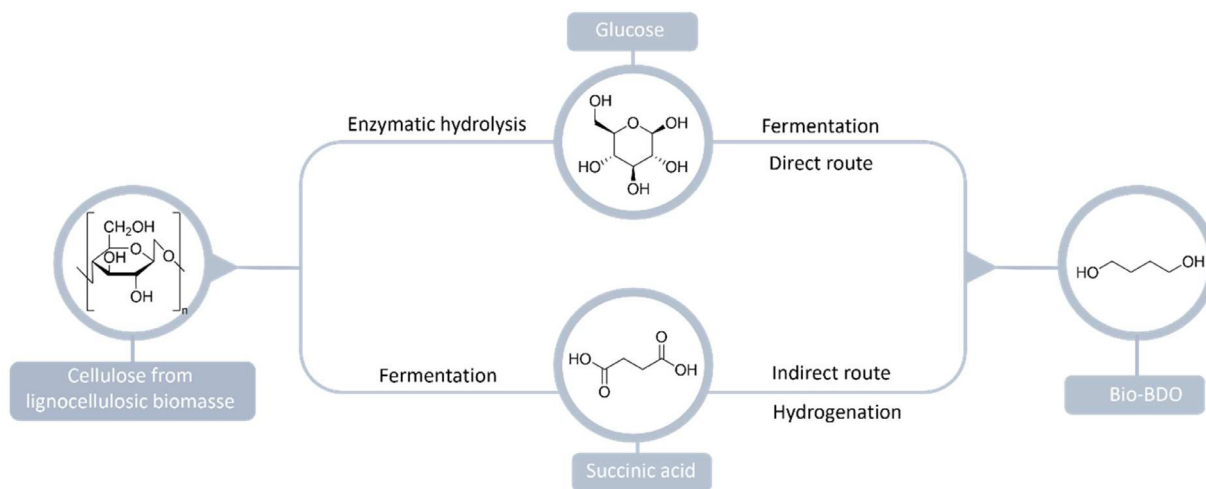


Fig. 3. Chemical structure of common short diols.



Scheme 7. Schematic diagram for bio-BDO production from cellulose.

making it easy to supply [66]. It is different from difunctional short polyols, since it is composed of three free hydroxyl-groups. Most of the time, glycerol is used as a chain extender for PU thermosets formation. Since glycerol has a low molecular mass ($92 \text{ g}\cdot\text{mol}^{-1}$), the addition of only a small amount in the formulation is necessary to crosslink a PU-based system.

3.1.2. Natural oil polyols

For several decades, vegetable oils have been gaining popularity due to their specific structure and their possible response to sustainability concerns. They are triglycerides i.e., esters of glycerin and fatty acids among which, five are commonly found: palmitic (C16:0) and stearic (C18:0) acids, that are saturated, and oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) that are unsaturated (Fig. 4). As such, vegetable oils carry multiple reactive sites such as double bond and carbonyl groups, making them good candidates to design bio-based polyols. Moreover, some vegetable oils have natu-

rally reactive functions towards isocyanates such as hydroxyls (castor and *lesquerella* oil) or epoxy groups (*veronia* oil).

In addition to these chemical advantages, the large availability and the low price of vegetable oils make them very attractive for industrial applications.

Among vegetable oils, one of the best choices to synthesize PU is castor oil because it is non-edible and naturally has three hydroxyl groups in addition to the unsaturations. Global production of castor oil plant is concentrated around a small region of India called Gujarat. It is also cultivated in Africa and South America, but India is known as the world leader in castor oil production and leads the international market with approximately 250 kt and 350 kt of production per year [67]. Several companies obtain supplies of castor oil from Indian growers and can thus tailor their own polyols [68–70]. Because of its natural hydroxyl functionality, castor oil is used in PU-based thermosets formulations. Even if the hydroxyl pending groups are secondary alcohols, castor oil has sufficient reactivity to crosslink a system. Thermosets which

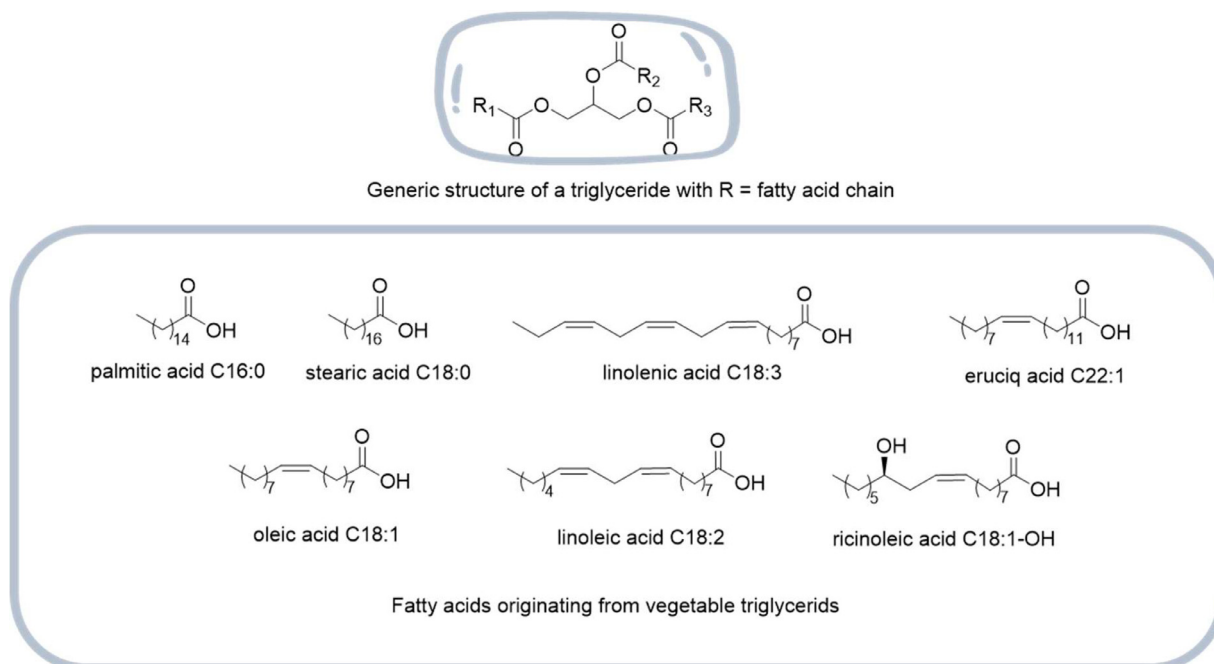


Fig. 4. Structure of various triglycerides.

Table 3
Main producers and products of natural oil polyols [72,73].

Producer	Location	Trade name	NOP	Bio-content	F
Alberdingk boley	USA	Albodur®	Castor oil	100%	
BASF polyurethane	Germany	Sovermol®	Soybean oil	65-100%	2 – 3.5
Bio-based technology (Acquired by Cargill in 2017)	USA	Agrol®	Soybean oil	99%	2-7
Cargill	USA	BiOH®	Soybean oil	87-98%	1.3-2
Dow	USA	Renuva™	Soybean oil	NA	NA
Emery oleochemicals	Malaysia	Emerox®	Palm oil	45-99%	1.1-4.7
Exaphen	Germany	Exaphen®	Cardanol	73-99%	3-8
Hokoku's oil	Japan	NA	Castor oil	NA	2-5
Huntsman	USA	Jeffadd® B650	Soybean oil	65%	2-6
Itoh oil chemicals	Japan	Uric®	Castor oil	NA	2-3
Jayant agro-organics	India	Jagropol	Castor oil	NA	NA
Musim Mas	Malaysia	PK	Palm oil	87%	NA
Oléon	France/Belgium	Radia®	Various	100	2-2.2
Polylabs	Latvia	BioPolyol®	Rapeseed oil Tall oil	70-83	2-2.1
Stahl	USA	Relca Bio®	Rapeseed oil	56-61%	2
Vertellus	USA	Polycin™	Castor oil	100	2.2-2.7

are designed with castor oil have a low glass transition temperature (T_g), the network meshes being wider and more flexible than the ones designed with glycerol [71].

On the other hand, soybean, rapeseed, linseed, and sunflower oil are the most produced vegetable oils and thus the most affordable for a large-scale production. Many companies propose polyols derived from several vegetable oils; some of them are listed in Table 3.

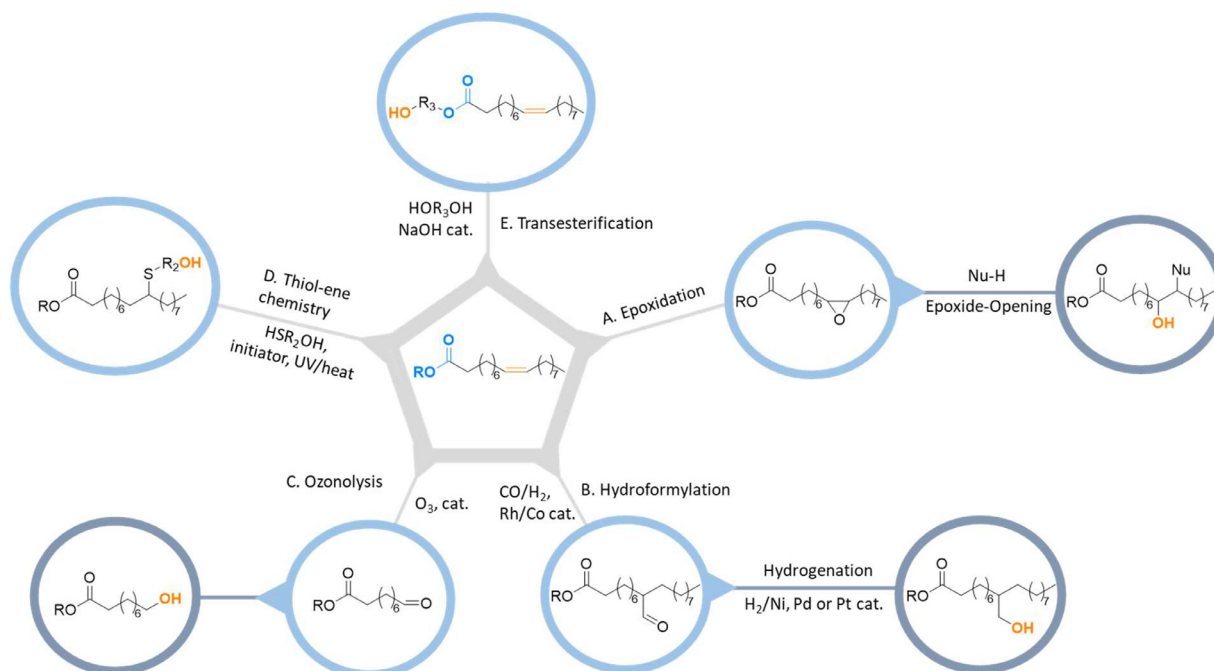
At laboratory scale, it is possible to design reactive vegetable oils through the functionalization of the C-C double bonds. The synthesis of polyols derived from vegetable oils enables controlling the functionality and the exact structure of the final compound. Moreover, some chemical modifications lead to primary alcohols that are more reactive than the secondary alcohols carried by castor oil.

Among these reactions, epoxidation of the unsaturation (Scheme 8-A) followed by the opening of the epoxy ring with a nucleophile like an alcohol or an amine lead to the production

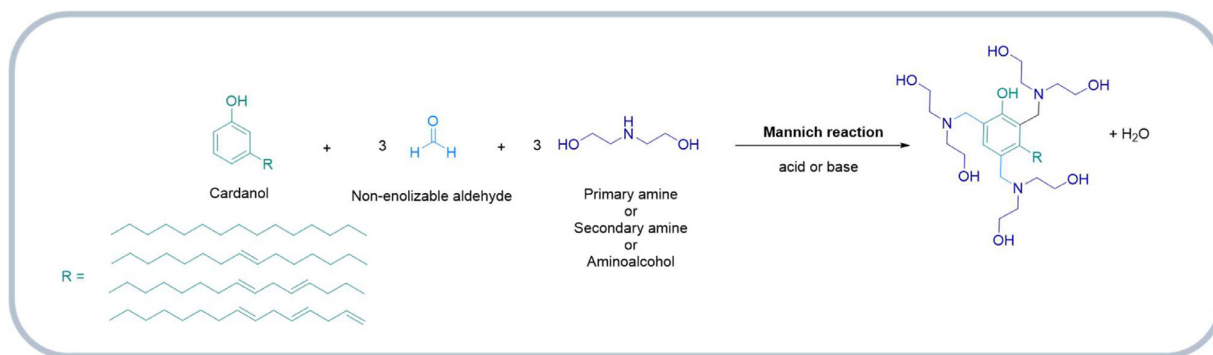
of oils with potentially more than 3 secondary alcohols. Epoxidation of vegetable oils [74] involves an organic peracid, usually performic or peracetic acid. Given the instability of organic peracids, it is safer to produce them *in situ* as a product of the reaction between hydrogen peroxide and a carboxylic acid. The reaction system is biphasic; the peracid synthesis will take place in the aqueous phase and the epoxidation reaction in natural oils phase [75-77].

The hydroformylation of natural oil polyols enables the conversion of double bonds into aldehydes easily converted into primary alcohols by hydrogenation (Scheme 8-B). It thus offers the opportunity to synthesize more reactive natural oil polyols than castor oil. The hydroformylation can be performed in the presence of rhodium catalyst at 110°C, with a gas mix of carbon monoxide and dihydrogen [78,79].

Ozonolysis of vegetable oils involves two steps (Scheme 8-C). The first one enables the formation of ozonide at the unsaturated sites of vegetable oils. Simultaneously, the decomposition of



Scheme 8. Summary of the reaction routes for the synthesis of NOPs from vegetable oils [84]. Copyright 2023. Adapted with permission from Edition Diffusion Press sciences.



Scheme 9. Mannich reaction and an example of CNSL-based Mannich base.

ozonide into aldehyde and carboxylic acid occurs. Then, reduction of the aldehyde function into alcohols in the presence of a Raney nickel catalyst [80] is performed to produce di or trifunctional polyols. Ozonolysis was performed on soybean oil, rapeseed oil and synthetic triglycerides to obtain polyols containing primary alcohols with high reactivity. However, it should be noticed that this technique only allows the production of polyols with a functionality lower than 3, which can be detrimental for PU thermoset synthesis.

Thiol-ene chemistry involves a free radical mechanism allowing thiols grafting onto double bonds (Scheme 8-D) [81,82]. The thiol-ene approach enables the synthesis of compounds containing primary alcohols, which are known for their high reactivity. This technique seems much easier to implement since it involves only one step, doesn't necessitate the use of a metal catalyst, and has no limitations concerning the nature of the raw materials. Furthermore, there is a wide variety of thiol compounds with diverse structures readily available.

Contrary to the previously mentioned chemical modifications, transesterification has a different approach (Scheme 8-E). This technique uses the ester bonds of the vegetable oil to produce polyols. Typically, an alcohol in excess, such as glycerol or pentaerythritol [83], is used to react with the oil in the presence of a small amount of catalyst. Although quite simple to implement, this technique gives rise to a polyol with all OH functions grouped at the end of a long pendant alkyl chain, which can impart low T_g in the final PU.

To summarize, the development of oleochemicals can be carried out with two different approaches: the double-bond modification of crude oils or fatty acid derivatives and the ester bond modification of vegetable oils [85]. The chosen functionalization path determines the final properties of the polyol (primary, secondary, or tertiary alcohol, functionality, hanging functions) and therefore, of the final PU material. For example, increasing the functionality of the modified vegetable oils, leads to more cross-linked networks, resulting in high T_g materials.

Despite the low cost of starting material (vegetable oil), it should be noticed that these functionalization processes require, most of the time, a two-step reaction employing expensive catalysts and toxic/dangerous reagents. These drawbacks limit the transfer of these methods to an industrial scale. Moreover, polyols obtained from vegetable oil can have a distinct odor, leading to certain challenges for industrial applications. For instance, Ford Motor Company collaborated with Lear Corporation and Urethane Soy Systems Company to develop a 40% soy-based polyurethane foam [86–88]. To address this concern, Ford Motor Company devised a new synthesis process based on ultraviolet light instead of high heat and catalysts to prevent the formation of byproducts and the development of a musty odor. Currently, the actual PUF is created by combining a blend of soy-based and petrochemical-based

polyols along with petrochemical-based isocyanate and additives. By using soy-based foams in their vehicle seats, Ford demonstrates the efforts that industries are making to develop greener alternatives using vegetable oils.

3.1.3. Mannich polyols from renewable raw materials

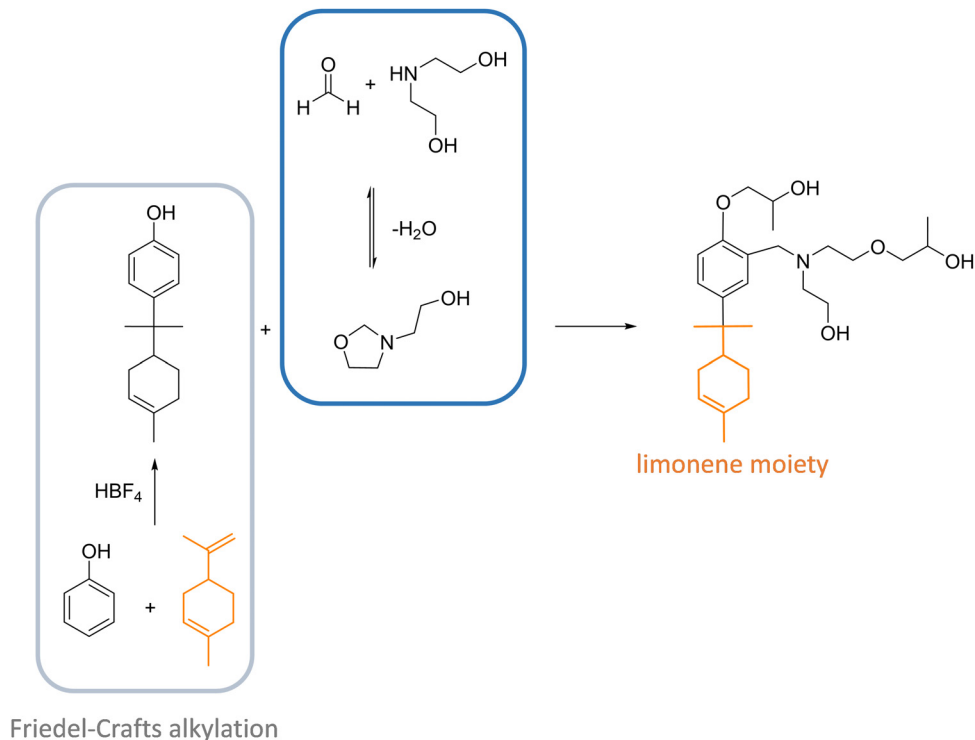
Mannich polyols is a family of aminic polyethers polyols that include an aromatic structure. Its synthesis consists in an amino alkylation of an enolizable carbonyl compound (α -CH acidic compound) with a non-enolizable aldehyde (usually formaldehyde) and an amine or an aminoalcohol also known as Mannich base [89]. The use of aminoalcohols instead of amines leads to the formation of aminoalcohol-carbonyl compounds named Mannich polyols (Scheme 9). Mannich polyols have an autocatalytic reactivity due to the presence of tertiary amines (basic catalyst) in their structures. Therefore, Mannich polyols are sufficiently reactive towards isocyanates without the need of catalysts [90]. Bio-based Mannich polyols can be obtained from the chemical modifications of cardanol. Cardanol is a molecule found in cashew nutshell liquid (CNSL), a by-product of cashew nutshell production. This is a cheap and an available renewable resource material. More precisely, the main components of CNSL are: anacardic acid (60–65%), cardol (15–20%), cardanol (10%) and methyl cardol [91].

Recently, industrial bio-based Mannich polyols from CNSL industry were developed by Cardolite Corporation [90–92]. Cardolite Corporation is an American manufacturer of products derived from CNSL which proposes six different Mannich polyols under the tradename GX from 9101 to 9106 with an average functionality of 3–4. These products are colorful, from red to brown liquid and have a viscosity between 1,550 and 13,000 cPs at 25°C [93].

Mannich polyols are mostly used for the synthesis of rigid polyurethane “spray” foams that have a very high T_g between 50°C and 110°C [94]. Indeed, the aromatic ring and the high functionality of these molecules help to obtain rigid materials. On another hand, the high reactivity, the good fire resistance and the thermal resistance make them suitable for PUF applications. Moreover, it is an accessible and mature product since Cardolite has commercialized different grade of Mannich polyols from CNSL. However, the products are not 100 % bio-based and some of them can be difficult to add in pumped formulations due to their high viscosities.

Industries are not the only one who take great interest in Mannich polyol to design PU materials. In 2015, Gupta *et al.* [90] reported the synthesis of a novel limonene based Mannich polyol. Limonene is an abundant and inexpensive natural compound from citrus industry. This monocyclic terpene with one internal and one external double bond is a very good substrate for a large scope of chemistries involving double bond reactions. During this study, limonene based Mannich polyols were synthesized by an easy three steps reaction represented in Scheme 10.

Synthesis of 1,3-N-hydroxyethyl oxazolidine



Scheme 10. Possible structure of limonene based Mannich polyols obtained through a three-step synthesis.

Then, the preparation of rigid PUFs was achieved by blending the Mannich polyol with two others less reactive and commercial polyols and with a methylene diphenyl diisocyanate. Thermal and mechanical analyses indicated that this rigid PU foams have a very high T_g around 200°C. These foams also have high compressive strength (267 kPa) and very regular cell structure.

3.1.4. Bio-based lignin-derived polyols

Lignin is a natural polyol and a promising candidate for producing bio-based PUs. On average, lignocellulosic biomass contains 35–50 % cellulose, 20–35 % hemicellulose and 10–25 % lignin [95], making lignin abundantly available in nature.

They are different lignin extraction processes which all derived from papermaking industry. These chemical processes are carried out in two steps to separate lignocellulosic polymers: (i) liberation and solubilization of hemicellulose and lignin in the form of “mill black liquor”, (ii) filtration of insoluble cellulose and concentration of “mill black liquor”.

Usually, the lignin waste from papermaking industry (*i.e.*, mill black liquor) is burned as low-grade fuel [96,97]. Consequently, lignin is used as its lowest value and goes back directly in the carbon cycle. It is thus essential to value this renewable, biodegradable and environmentally friendly resource.

In nature, lignin is polymerized by plants from three monolignols: sinapyl, *p*-coumaryl and coniferyl alcohol, represented in Fig. 5.

Very few studies have used depolymerized lignin to produce polyols for PU synthesis. Nevertheless, different methods have been reported to transform lignin into polyols like oxypropylation [98], chemical grafting [99], heat treatment [100] or microwave liquefaction [101].

More recently, lignin was used without any modification or pre-treatment to improve economic aspects and preserve energy consumption [102]. In this work, PUFs were synthesized with 20 %^{wt} of lignin in the presence of polyether polyol as copolyol and a diisocyanate. In total, 15 different unmodified lignin were tested and approved. The lignin-based PU foams synthesized had high ther-

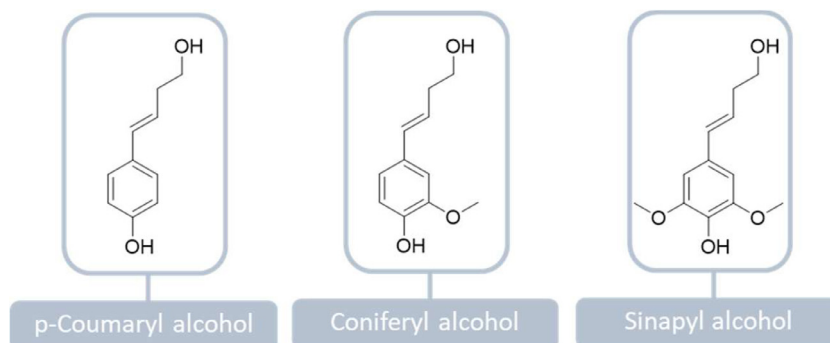


Fig. 5. Main components of lignin.

mal stability (temperature at maximal degradation = 377-395°C) and high tensile strength (tensile strength = 51-84 kPa). These properties are slightly different from batch to batch depending on the plant source or the preparation process. The characteristics of lignin samples thus must be checked and controlled before using it as a raw material for PU formation. Nevertheless, this study demonstrates the potential of lignin to partially replace fossil fuel-based polyols in the formulation of PU foams.

Researchers are not only focusing on foams but also on elastomers. Li *et al.* [103] synthesized lignin-based polyurethane elastomers (LPUe) with high toughness, tensile strength, and high modulus by using unfunctionalized lignin. In this study, two types of lignin with two different molar masses (600 and 3600 g·mol⁻¹) were reacted with poly(propylene glycol) tolylene 2,4-diisocyanate. When the content of lignin (600 g·mol⁻¹) in LPUe increased from 5 %wt to 40 %wt, T_g of the LPUe increased from -44°C to 8°C. Besides, slight increase of the T_g from -47°C to -36°C was observed when using the 3,600 g·mol⁻¹ lignin instead of the 600 g·mol⁻¹ lignin. Similarly, it was found that thermal stability of the LPUe increased with lignin content, in correlation with the aromatic ring content.

These results highlight the potential application of lignin in the preparation of partially bio-based PU materials. Nevertheless, using lignin for PU production is still in its infancy and further research has to be done in order to demonstrate its full potential. In addition, there is no product from lignin that has been launched by industries or that is commercially available.

Lignin can also be used to obtain significant economic and environmental compounds such as vanillin [104,105]. Vanillin is a fully bio-based component that can be used to synthesis bio-based PU. As reported by several groups around the world. For example, Xu *et al.* [106] synthesized a series of bio-based and healable PUs in absence of any solvent and catalyst from vanillin and L-tyrosine. Gang *et al.* [107] used a divanillin-based chain extender to obtain high performance PU. Wang *et al.* [108] prepared a chain extender from acetylation of vanillin and glycerol to design PU systems. These examples (Fig. 6) highlight the ability of vanillin to act as a valuable precursor for bio-based PU synthesis through simple chemical modifications.

Vanillin is a particular example of a lignin-derived product. There are many other examples that could be considered to obtain diols or polyols and thus reactive compounds for PU synthesis, such as resveratrol, eugenol [109,110], guaiacol [111], bisguaiacol F or triphenols [112]. For some of them, their uses in PU systems still need to be proven.

3.2. Macromolecular bio-based and low impact polyols

3.2.1. Polyester polyols

Used for more than 75 years in PU industry, polyester polyols are hydroxyl-ended macromolecules containing several ester groups in their backbone [113]. Usually, they were industrially prepared by step-growth polymerization of diols and diacids or anhydrides [114]. A broad product catalogue is proposed by suppliers to synthesize material-based PU with specific properties depending on the selected polyester polyol. Polyester polyols with an aromatic moiety are synthesized using low-cost building blocks such as terephthalic acid, phthalic anhydride or crude recycled polyethylene terephthalate and low-cost diols such as EG, DEG and polyethylene glycol (PEG) among others. They provide remarkable properties to the resulting materials such as good hardness values, abrasion resistance and hydrolytic stability. On the other hand, polyester polyol that are manufactured by using a diversity of dicarboxylic acids such as adipic acid and linear diols such as PDO, MPDO, BDO, EG, DEG, propylene glycol or co-diol polyol EG/BDO copolyester, provide more flexible materials [58].

To obtain bio-based polyester polyols, bio-based diols and diacids obtained from renewable resources can be used. Indeed, as explained in Section 3.1.1, short bio-based diols and diacids have been recently developed by different companies, such as Biosuccinum™ (succinic acid) by Roquette and DSM, Oleris® bio-based sebacic acid by Arkema [115], as well as bio-based adipic acid and bio-based BDO by Genomatica. A non-exhaustive list of different producers of bio-based diols and diacids is given in Table 4.

As an industrial example, Gantrade has developed a product line of bio-based linear polyester polyols that contain 100 % of renewable content. To this end, they used bio-succinic acid and bio-sebacic acid (Scheme 11) as the aliphatic diacids and bio-PDO and bio-BDO as bio-based diols [116].

Evonik developed partially bio-based polyester polyols known as DYNACOLL® 7000 for PU synthesis. Emery Oleochemicals has developed Emerox® polyester polyols with a high bio-based content (ranging from 44 % to 99 %) and variable functionality (2-3.7) and viscosity [117]. Synthesia Technology has developed bio-hoopol polyesters polyols with varying bio-based content (ranging from 30 % to 100 %) and different viscosities [118]. The industrial availability of short bio-based diols and acids provides a strong boost to synthesize bio-based polyester diols. The large scope of diols and acids allows to design polymers with different proper-

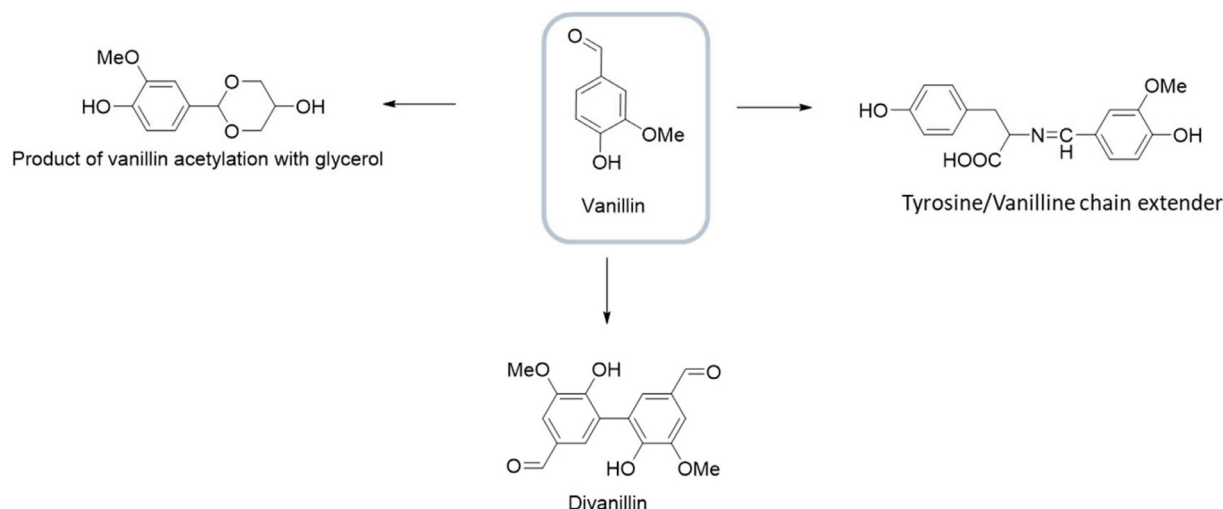
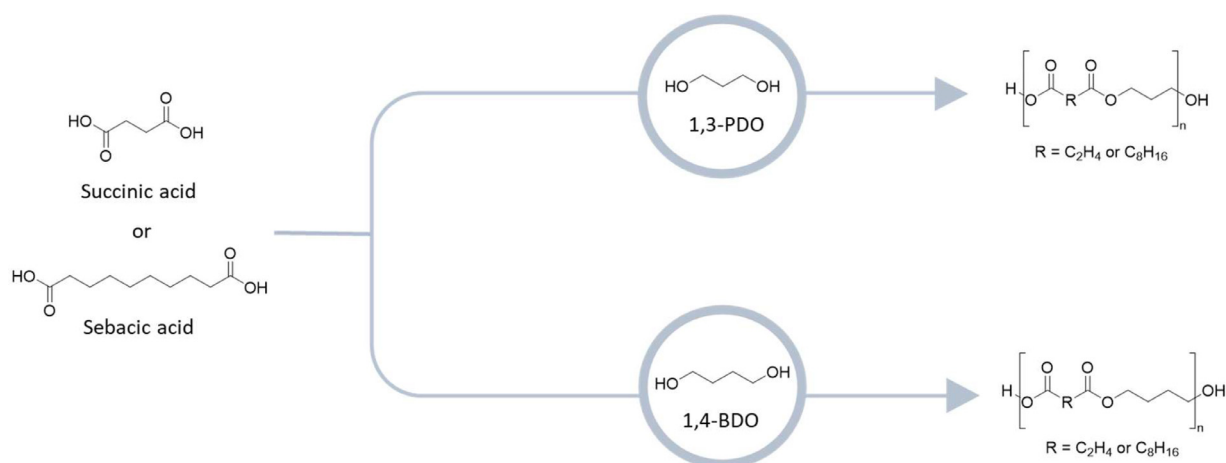


Fig. 6. Examples of vanillin-based products used to design PUs.

Table 4
Summary of bio-based diols and diacids producers.

Company name	Bio-based product	Involved process
BioAmber	Butanediol	Hydrogenation of bio-based succinid acid
Genomatica	Butanediol	Fermentation process of crop-derived sugars
Metex Noovista	1,3-propanediol	Fermentation process of rapeseed plant
Dupont Tate & Lyle Bio products	1,3-propanediol	Fermentation of corn sugar
Gantrade	Butanediol, 1,3-propanediol and succinic acid	Fermentation of corn sugar
Genomatica	Sebacic acid	Saponification of castor oil with caustic soda
DSM and Roquette	Adipic acid	Fermentation process of soybeans and oil palm fruits
	Succinic acid	Low pH yeast process

**Scheme 11.** Bio-based polyester polyols from succinic acid or sebacic acid.

ties. Therefore, bio-based polymers can exhibit similar properties than petrochemical-based ones or even enhance them.

A different strategy to obtain bio-based polyester polyol is by ring-opening polymerization (ROP) of cyclic esters such as lactide (Scheme 12) to produce poly(lactic acid) (PLA) [119], well-known for its use in bio-plastic conception.

PLA is produced from renewable feedstocks like sugarcane, corn, sugar beet and cassava [121]. PLA is biodegradable under certain conditions, compostable or chemically recyclable (depolymerization) [122]. Natureworks, a company based in Minnetonka, Minnesota, is one of the world's leading manufacturers of PLA. Additionally to its regular extrusion and injectable PLA grades, this company launched Vercet™, a product line corresponding to lactide-based chemicals such as polyester polyol used in PU applications including coatings, adhesives, sealants, and elastomers [123]. Vercet™ lactide-based polyols can be used to design a large variety of PU materials since they exhibit different performances. Vercet™ grade P1025X is used as a chain stopper since it is a monofunctional polyester alcohol. Vercet™ grade P3025X is a trifunctional polyester polyol and is used as crosslinker. Vercet™ also proposes difunctional lactide-based polyester polyols. In total, Na-

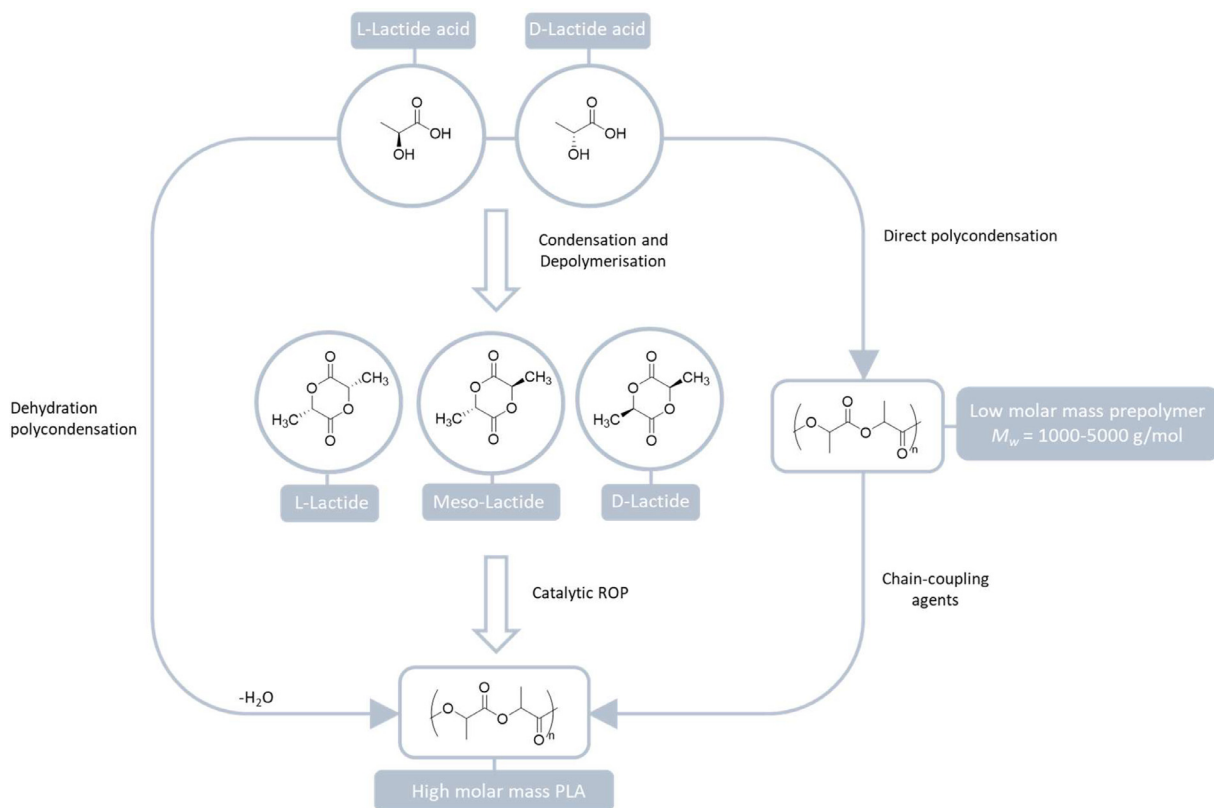
tureworks proposes eight different grades of PLA-derived polyols with different functionality, T_g and viscosities (Table 5).

In a study made by Natureworks, PUs were formulated with two different grades of Vercet™, P2040X and P2140X, which are quite similar in terms of molar mass, functionality and T_g . Methylene diphenyl diisocyanate was used to cure the system and was found to contribute to the high hardness (around 86 ShA with P2040X and 84 ShA with P2140X) of the material since it is an isocyanate with two aromatic rings. Both materials have a T_g around 50°C. In each case, Vercet™ polyols provided high solvent resistance, excellent oil resistance, hardness and toughness to PU materials. It can be an excellent option to design bio-based and biodegradable PUs. Industrial projects related to PLA production are expected to strongly grow in all parts of the world [124–127].

Since PLA is a polymer containing ester bonds, it can be chemically transformed by alcoholysis and glycolysis through the transesterification reaction. As it will be explained in part 7.3, PU materials can be subject to chemical treatments to positively manage their end-of-life. In this same purpose, PLA resin, *i.e.* high molar mass chains, can be transformed into lower molar mass chains terminated by alcohol functions. Academics teams have al-

Table 5
Properties of Vercet™ alcohols.

Grade	T_g (°C)	Functionality	Viscosity at 100°C (mPa.s)	Hydroxyl value (mg KOH/g)	Calculated molecular mass (g·mol ⁻¹)
P1025X	15	1	1,200	25	~2,200
P20112X	5	2	<1,000	112	~1,000
P2056X	25	2	2,100	56	~2,000
P2040X	32	2	3,700	40	~2,800
P2025X	40	2	11,300	25	~4,500
P2140X	22	2	1,800	41	~2,750
P2125X	30	2	7,500	25	~4,500
P3025X	40	3	19,100	29	~3,900



Scheme 12. Synthetic pathways to PLA (adapted from [120]).

ready demonstrated that PLA wastes can be valued into reactive low polyols and used to design PU materials. Most of the time, to achieve depolymerization of PLA resin through transesterification route, an active hydrogen compound and a transesterification catalyst must be used. For example, J. Paciorek-Sadowska *et al.* [124] synthesized an oligomeric polyhydric alcohol from PLA wastes by using diethylene glycol and anhydrous zinc stearate as catalyst. This raw material was used to prepare PU foams exhibiting similar properties as commercially available foams. Eang *et al.* [128] also designed hydroxyl-ended products from PLA wastes with two different alcohols (propylene glycol, and 1,4-butanediol). They used these alcoholized products to design PU materials that exhibit self-healing properties by heat treatment at 60°C. Nevertheless, it can be really challenging to collect PLA wastes from sorting centers since PLA recycling loop is not well established in Europe or in other countries.

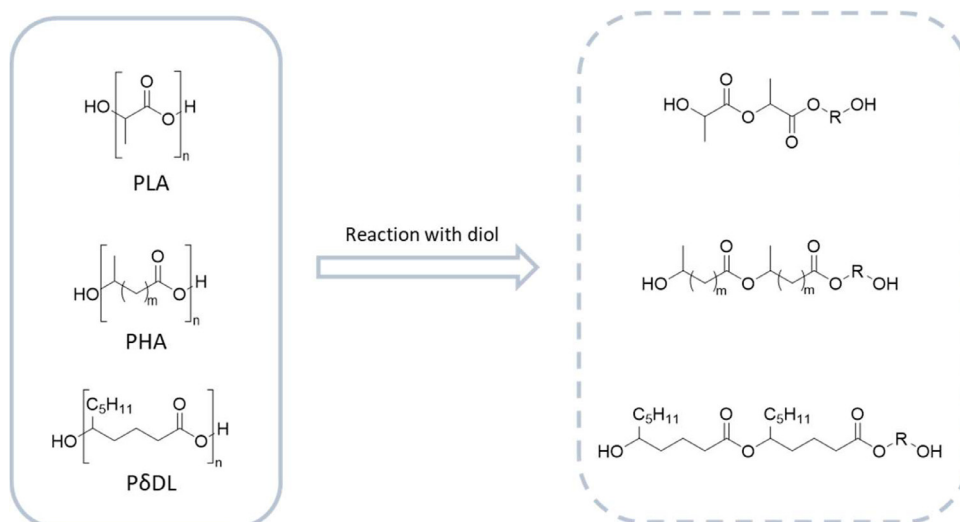
Polyhydroxyalkanoate (PHA) and poly(δ -decalactone) (P δ DL) are also bio-based and biodegradable polyester polyols. As such, they can also be employed for the production of polyester polyols. PHA is produced in nature by numerous micro-organisms through bacterial fermentation of sugars or lipids and δ -decalactone naturally occurs in fruits (coconut, raspberry) and milk in small quantities and can be also synthesized from fungi. P δ DL is obtained by the ROP of δ -decalactone. As PLA, PHA and P δ DL polymers can be depolymerized by alcohols compounds to obtain reactive raw materials. Academic teams showed that as PLA-based polyols, PHA and P δ DL-polyols obtained from depolymerization steps can be used to formulate PU material with tunable properties. An example of the final structures that can be obtained from depolymerization of PLA, PHA and P δ DL are illustrated in Scheme 13. These structures are idealized examples and do not reflect reality since the depolymerization step results in a mixture of polyols of different molar masses [128].

Depolymerization of polymers by transesterification route can be transposed to multiple candidates bearing ester bonds in their structures. It is a sustainable way to make reactive polyols from wastes and to design raw materials with different molar mass depending on polyester, alcohol ratio, alcohols nature, catalyst nature, temperature of reaction or/and reaction time. However, governments have not taken measures to collect PLA or PHA-based PU to recycle them.

3.2.2. Polyether polyols

Polyether polyols are the most common polyols employed to prepare PUs. Almost 75 % of polyols used in PU industry are polyether polyols compared to polyester polyols that represent 25 %. Polyether polyols offer hydrolytic stability and flexibility but are sensitive to oxidation. They are formed from the exothermic ROP of oxiranes such as ethylene oxide (EO), propylene oxide (PO), butylene oxide (BO), or tetrahydrofuran (THF). EO, PO, BO or THF are petrochemical-based ingredients available in large amounts and at a low cost, making them good candidates for industrial scale production of polyether polyols [1,29,129]. To polymerize oxiranes into polyether polyols, it is necessary to use a short chain polyol as initiator. The functionality of the initiator will determine the polyether final functionality. Most of the time, initiators are fully bio-based, like glycerol, sorbitol, pentaerythritol, trimethylolpropane or even sucrose [130]. Even though these initiators are bio-based, the resulting polyether polyols cannot be defined as bio-based because of the petrochemical origin of monomers [131]. Bio-based polyether polyols have thus been developed by step-growth polymerization of short-chain bio-based diols.

Following this strategy, BASF developed bio-based polyTHF derived from 1,4-BDO. The bio-based polyTHF is claimed to be identical to the petrochemical-based one [132]. Besides, the Weylchem group developed its own bio-based polypropanediol (PO3G) under



Scheme 13. Examples of idealized final structures of PLA, PHA and P δ DL depolymerized polyols.

Table 6
Technical specifications of Velvetol® and Ecoprool.

Grade	Molar mass (g·mol ⁻¹)	Viscosity at 40°C (mPa.s)	Density at 40°C (g.cm ⁻³)	Melting point(°C)	Hydroxyl value (mg KOH/g)
Velvetol H250	200-300	40-60	1.030	<0	370-550
Velvetol H500	400-600	90-120	1.020	0-5	280-187
Velvetol H1000	900-1,100	200-300	1.018	12-14	125-102
Ecoprool 1000	900-1,100	400-600	1.018	12-14	124.6-102.0
Velvetol H2000	1,900-2,100	750-900	1.016	16-18	59.1-53.4
Ecoprool 2000	1,900-2,100	1,700-1,900	1.016	16-18	59.0-53.4
Velvetol H2700	2,600-2,800	1,550-1,850	1.016	22-25	43.2-40.1

the trade name Velvetol® from bio-based 1,3-PDO thanks to a microorganism process. Furthermore, 1,3-PDO is used as a building block to produce a wide range of high-performance polyether polyols since Velvetol® is available in five different grades, H250, H500, H1000, H2000 and H2700 that have increasing molar mass, hydroxyl equivalent weight and viscosity with their nominative number (Table 6) [133].

The molar mass of Velvetol® grade will have a huge impact on the final properties of PU materials. If Velvetol® is used to elaborate thermoset materials, grades H250 and H500 give a denser network with a higher T_g . On the contrary, with grades H2000 and H2700, the network is looser and the T_g decreases. Velvetol® can also be used to design TPU. However, the conclusions are the same regarding molar mass, flexibility/rigidity and T_g tendency.

A Korean company, SK chemicals, also developed bio-based PO3G named Ecoprool [134]. They propose two different grades, Ecoprool 1000 and 2000, which present the same technical specifications than Velvetol H1000 and H2000 except in terms of viscosity.

Another natural molecule derived from the cereal industry that can be used to design high performance polymers, is 1,4:3,6-dianhydrohexitol also named isosorbide. Isosorbide is a glucose-derived molecule with a rigid, chiral structure and with no toxicity risks. Roquette is one of the companies that offers the largest range of sugar alcohols including isosorbide, sold under the tradename Polysorb. Isosorbide is also commercially available from Archer Daniels Midland Company. Academic works show the possibility to incorporate this monomer into PU materials by two different ways: synthesis of isosorbide-based polyether polyol by ROP [135] or incorporation as a chain extender [136]. Regarding the first option, it allows tailoring polymer architectures from isosorbide by controlled ROP. However, the method can difficultly be transferred to

industrial scale due to the many synthesis steps. The use of isosorbide as a simple compound for TPU synthesis is therefore more promising. Blach *et al.* used a 4,4'-diphenylmethane diisocyanate (MDI) terminated polyester polyol prepolymer and isosorbide as chain extender. This model was compared to the model where BDO is used as chain extender. Among all the analysis performed, T_g of the isosorbide-based samples were all around -45°C instead of -50°C for BDO-based samples. Consequently, isosorbide contributes to an increase in T_g values. However, the secondary nature of the hydroxyl groups and the internal hydrogen bonds drastically decrease isosorbide reactivity, which can be a drawback. The high price of this compound can explain why, until now, no industrial group has shown interest in the production of isosorbide-based polyols.

3.2.3. Low carbon footprint polycarbonate polyols

Polycarbonate polyols are hydroxyl-terminated polymer containing repeating units with a carbonate group in the main chain. One attractive method to synthesize polycarbonate polyols is by copolymerization of carbon dioxide and epoxides, as discovered by Inoue in 1969 [137]. The advantage of this method is the use of nontoxic and inexpensive CO₂ as a sustainable carbon source. Polycarbonate polyols obtained by this method can contain up to 50 % of CO₂ [138]. Therefore, they have a very low carbon footprint and allow the use of less fossil-based feedstocks.

Cyclohexene oxide and propylene are two of the most investigated epoxides to form polycarbonate by reaction with CO₂. For instance, poly(propylene carbonate) and poly(cyclohexene carbonate) have been commercially synthesized from CO₂ by many companies such as Saudi Aramco [139], Empower Materials [140], Eonic Technologies [141], Covestro [142] and Repsol [143].

The most frequently utilized petrochemical-derived polycarbonate polyol in the PU industry is a product developed by Covestro, marketed under the trade name Desmophen®. It is manufactured through the reaction of 1,6-hexanediol and diphenyl carbonate [144–146]. Nevertheless, if diphenyl carbonate were sourced from greenhouse gases, it could present an attractive alternative for the production of polycarbonate polyol with a reduced carbon footprint. Several scientific articles [144,145] illustrate the potential for obtaining diphenyl carbonate from CO₂, thus emphasizing the viability of this approach.

Like polyester polyols or polyether polyols, polycarbonate polyols can be used to formulate PU-based materials. The functional groups in polycarbonate polyols are rigid, resulting in a high T_g .

Consequently, PUs based on polycarbonate polyols have a higher modulus and greater mechanical strength than those made with polyester or polyether polyols using the same system. Furthermore, due to the presence of an additional oxygen atom in the carbonate group of their backbone, they exhibit greater resistance to hydrolysis and oxidation when compared to polyester and polyether polyols.

3.2.4. Post-industrial recycled polyols

There are several types of polyols that can be obtained from post-consumer wastes recycling. These materials should be easy to collect and reprocess. Here are some examples: polyols based on recycled polyethylene terephthalate (PET), polyols based on recycled polyolefins, polyols based on recycled PLA and polyols based on recycled polyurethanes.

The widespread use of PET in packaging, coupled with its non-biodegradable nature, generates a significant amount of waste, especially in the form of plastic bottles. These wastes are easily collectible post-consumer products and can be used to produce polyols for polyurethanes through chemical treatment [147–149]. The PET recycling process involves the depolymerization of PET through alcoholysis using various depolymerization agents such as EG, DEG, PDO, BDO, glycerol, and others. The resulting post-alcoholized PET products are oligomers or oligoester diols/polyols with hydroxyl terminal groups, which can be further employed for polyurethane synthesis or can lead to the creation of entirely new polyester polyols through reactions such as esterification with carboxylic acids.

In the literature [150,151], numerous examples demonstrate the feasibility of using recycled post-consumer PET for the development of PU materials. PET-based polyols contain aromatic rings that enhance thermal and mechanical properties, imparting rigidity to the final material. However, PET-based polyols present several drawbacks, including high viscosity, rapid crystallization, and incompatibility with blowing agents [152]. One way to address these limitations is by mixing PET-based polyols with polyester polyols of different compositions [153].

Huntsman corporation established a new brand of aromatic polyester polyols called Terol®, which is based on the upcycling of scrap PET bottles that would have otherwise ended up in landfills or being incinerated [154,155]. Since 2014, Huntsman has utilized the equivalent of 5 billion PET bottles (500 mL) to produce 131,000 tons of Terol® aromatic polyester polyols in Texas. This ingredient is widely used in the production of MDI-based PU foam and is also a crucial component for spray PU foam and polyisocyanurate board systems. Terol® contains up to 60 % recycled waste and helps to reduce the environmental impact of plastic wastes.

Huntsman Corporation is not the only industrial player utilizing PET waste to produce environmentally friendly aromatic polyester polyols and polyurethanes. Covestro is a major player in this field with its Desmophen® Eco product range, which includes recycled PET-based polyols. BASF also offers polyol solutions derived

from recycled PET under the trade name Elastollan® [156], such as DuPont with Cerenol®, and the Rampf Group with RAKU® [157].

Polyolefins mainly include polyethylene (PE) and polypropylene (PP). PE can be categorized into low-density polyolefin density PE and high-density PE based on their distinct physicochemical attributes, including density, crystallinity, and mechanical strength. High-density PE and PP find extensive utility in the manufacturing of durable plastic items, such as containers, bottles, and furniture, ensuring long-lasting service. Conversely, low-density PE is employed in the production of disposable packaging and plastic bags, characterized by shorter lifespans and widespread use [158]. The degradation of polyolefins is an ongoing process, accelerated by high temperatures and mechanical stress. This process transforms PE and PP plastics into saturated steam hydrocarbons, diesel, naphtha, syngas, or other chemicals, which are subsequently recycled in the production of new plastics. For example, the Novolooop Company has developed a technology called Accelerated Thermal Oxidative Decomposition to break down post-consumer polyolefin plastics into various organic acid monomers, which are then used to create high-quality plastic furniture. Recent advancements in chemical treatment have also made significant strides in the upcycling of polyolefins [159]. Chemical upcycling of polyolefins can be classified into four distinct categories: oils and arenes, carboxylic acids, syngas, and carbon materials. Another chemical strategy aims to produce high-value and reactive compounds from polyolefin wastes. Indeed, polyolefins are inert polymers that require chemical pretreatment to generate functionalized recycled polyolefins. This approach to chemical modification holds great promise for expanding the scope of their applications. One specific method involves structural alterations through the functionalization of C-H bonds in polyolefins. For instance, introducing active functional groups like hydroxyl, carbonyl, amino, or halogen atoms into the olefin intermediates can significantly enhance their value and performance [160–164].

Procter & Gamble, with its licensed technology called PureCycle, is a company actively engaged in plastic recycling. Similarly, Agilyx [165], SABIC [166], BASF [167], and Covestro [168] are also companies involved in this mission. They likely utilize the recycling of PE and PP to produce chemicals that could potentially be employed in the synthesis of polyols. These are instances of proof of concept, but they could become a reality if major industrial pioneers put in significant effort into the valorization of plastic waste into high-value monomers such as diols or polyols.

As described in Section 3.2.1 on polyester polyols, thermoplastic polyester polyols like PLA can be recycled through chemical processes with the aim of obtaining low-molecular-weight and high-value products, such as diols or polyols.

Finally, polyurethanes can be recycled using various techniques described in Section 7 on end-of-life management. Some of these techniques enable the recovery of materials such as polyols from PU materials [26]. For example, Zagar *et al.* chemically recycled flexible PU foams through aminolysis to recover high-value polyols [169].

4. Different routes to reduce isocyanate environmental impact and toxicity

As mentioned in Section 2.1, the high reactivity and versatility of isocyanates makes them essential components for PU synthesis nowadays. However, with the current concerns about health and environment (REACH and the green chemistry principles) related to isocyanate use or synthesis, research groups and industries are intensively working on replacing toxic materials with safer alternatives and by using bio-based precursors. In this section, greener and safer alternatives to synthesize isocyanates (with design of chemical products and processes that reduce or eliminate the use

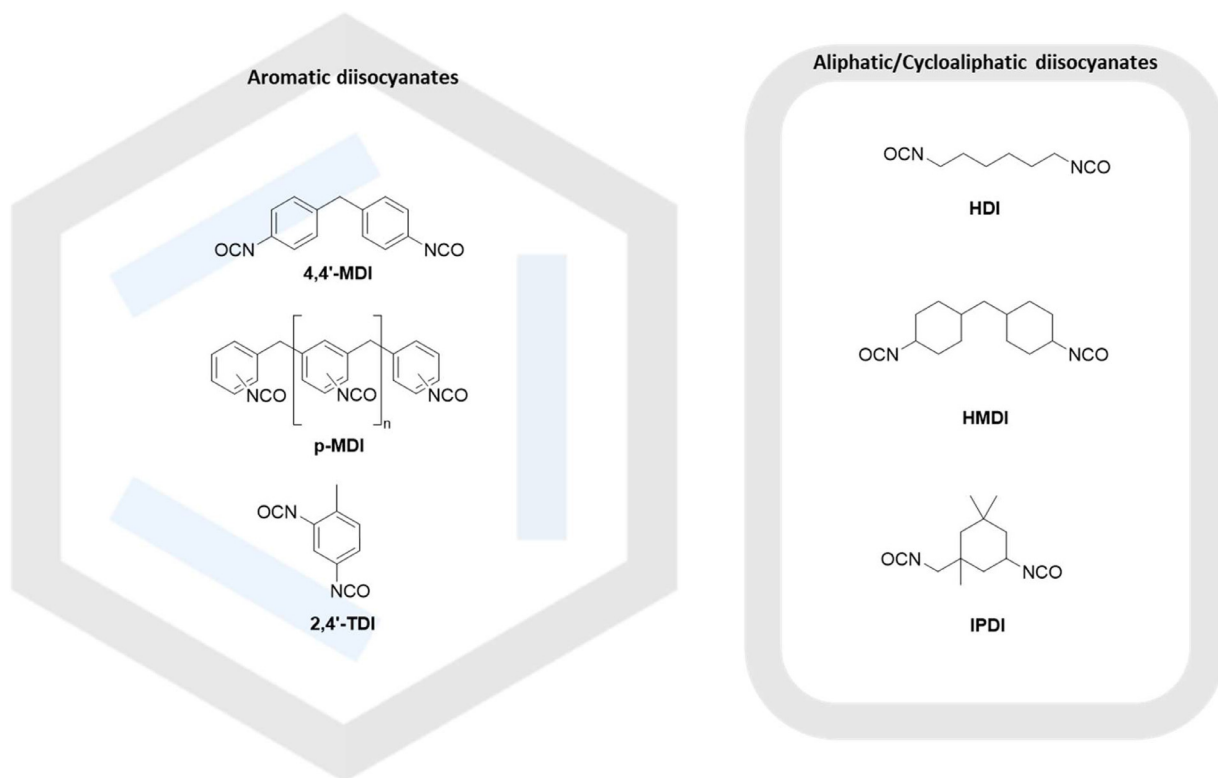


Fig. 7. Structure of the main petrochemical-based isocyanate compounds.

or hazardous substances) as well as strategies to reduce the isocyanate toxicity will be discussed.

4.1. Petrochemical-based isocyanates and non-phosgene routes to isocyanates synthesis

Isocyanates can be either difunctional or polyfunctional, aliphatic or aromatic (Fig. 7). The most important petrochemical-based aromatic diisocyanates are toluenediisocyanate (TDI) and MDI, mostly used as polymeric MDI. In most instances, TDI and MDI are available as mixtures of isomers that are mainly composed of 2,4'-TDI and 4,4'-MDI. Regarding aliphatic diisocyanates, the most industrially used are hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and hydrogenated MDI (HMDI) [129].

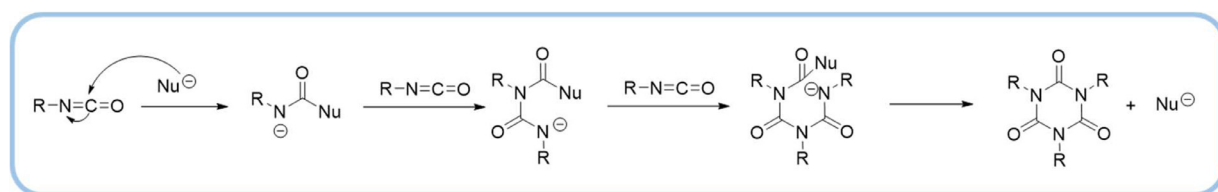
The ability of isocyanates to form polyfunctional structures such as isocyanurates by self-reaction is a common strategy employed at industrial level to obtain polyfunctional isocyanates monomers. To perform the trimerization reaction of isocyanates, it is essential to employ highly basic and nucleophilic catalysts such as trialkylphosphine. This reaction operates through a stepwise addition, as seen in Scheme 14. First, the catalyst adds, through a nucleophilic addition, on the carbon of the first isocyanate group, forming an amidate intermediate. The latter then reacts with the carbon of the second isocyanate group in a similar manner as the nucleophilic catalyst. After a third iteration of this addition step, attack

of the urea anion onto the carbonyl of the first isocyanate group closes the ring and releases the nucleophilic catalyst as well as the isocyanurate product [170]. Trimerization of difunctional isocyanates leads to the formation of free isocyanate groups that can eventually participate to a second trimerization. For this reason, it is important to control the self-condensation reaction of isocyanates to limit oligomerization reaction and viscosity increase.

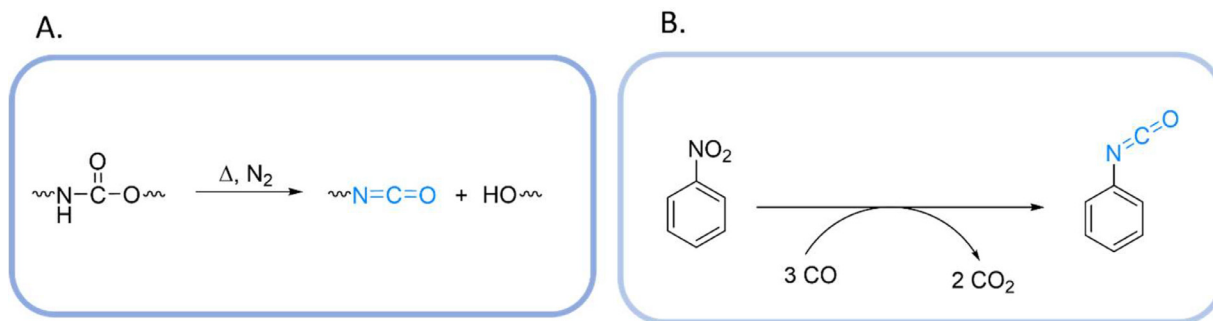
Polyfunctional isocyanates in the form of isocyanurates allow to enhance thermal resistance, chemical resistance, and flame retardancy. It also reduces the vapor pressure of isocyanate and hence decreases the final toxicity of the molecule.

As mentioned before, the great majority of isocyanates are produced *via* phosgene reaction. However, non-phosgene routes have been explored to forgo phosgene consumption. Three main pathways were developed but are still not economically competitive with conventional phosgenation, even if they could prevent from phosgene accidents. Thermolysis of urethane [171] (Scheme 15-A) and reductive carbonylation [172–174] (Scheme 15-B) are two processes that have in common the thermal decomposition of urethane into isocyanate and alcohol.

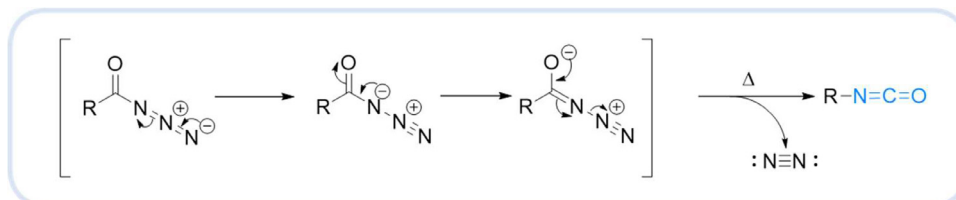
Thermolysis of urethanes is a very costly as it requires temperature above 300°C and a nitrogen atmosphere. Moreover, this method is limited by the volatility of the compounds and is not selective. The reductive carbonylation of nitro compounds is also energy consuming, a reaction temperature of 200°C and a carbon monoxide pressure of 85 atm being needed. Moreover, this reac-



Scheme 14. Reaction mechanism of the isocyanate trimerization to form isocyanurate catalyzed by a nucleophile.



Scheme 15. A. Thermolysis of urethane and B. Reductive carbonylation of nitrocompound.



Scheme 16. Reaction scheme of Curtius rearrangement.

tion is supported by rhodium or palladium catalysts and produces carbon dioxide as by-product. Other drawbacks of those reactions are the fact that the starting urethane used for the synthesis was probably obtained from an isocyanate derived from phosgene. Nevertheless, formation of urethane bonds by other routes than the isocyanate-alcohol addition reaction may provide for a sustainable and viable path to isocyanate.

For instance, TDI can be prepared by reaction of toluene diamine with dimethyl carbonate (DMC) followed by thermolysis of the urethane. DMC is a versatile chemical obtained from the oxidative carbonylation of methanol. The reaction requires high temperature, around 170°C. This synthetic pathway has also been studied to produce MDI, but as TDI production through urethane thermolysis, there is no economic viability. Conversion of isophorone diamine (IPDA) into IPDI via urethane thermolysis has been commercially performed and patented by Daicel Chemical, a Japanese company, proving the viability of this strategy. This non-phosgene process has a product yield of 93 % of IPDI with 1 % of isophorone monoisocyanate [175].

The third method to produce isocyanates without using phosgene is by Curtius rearrangement of carbonyl azides (Scheme 16), which was discovered in 1885 by Julius Wilhelm Theodor.

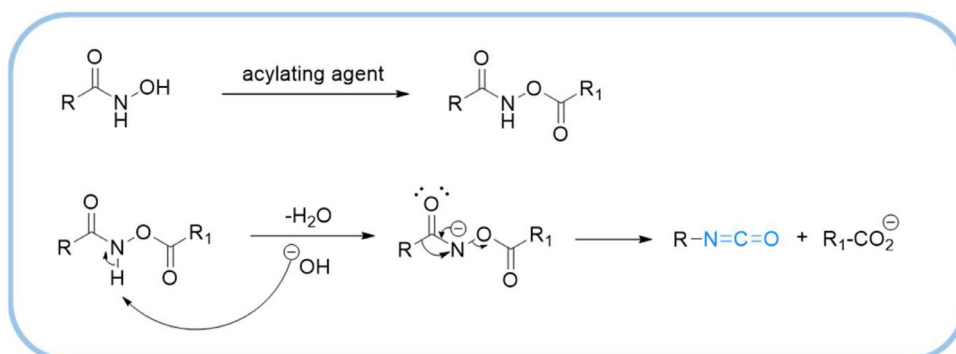
The reaction, triggered by thermal decomposition of the carbonyl azide [176–178], can be carried out with either aliphatic, aromatic, or heterocyclic compounds. Unfortunately, explosion hazards

related to the handling of azides make this reaction not viable for industrial processes.

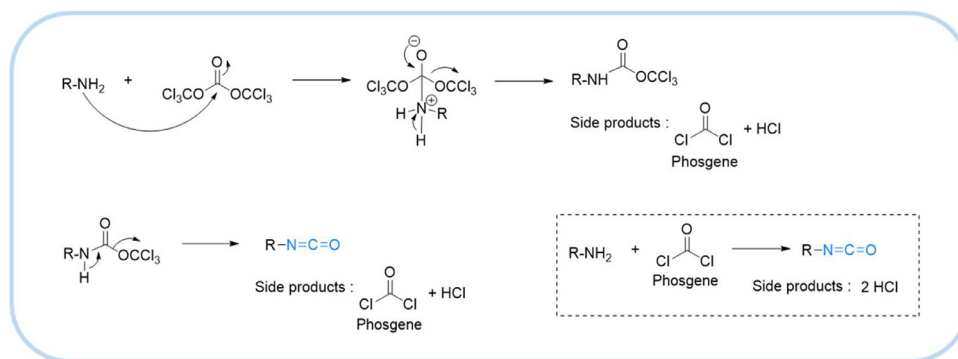
They are some other methods to synthesize isocyanate such as Lossen rearrangement [179] (Scheme 17), and the reaction of an amine with bis(trichloromethyl carbonate) *i.e.* triphosgene (Scheme 18) [180]. The single step reaction using triphosgene was explored to produce a difunctional isocyanate monomer from cardanol. This method is easy to implement at a laboratory scale since triphosgene is a solid. Nevertheless, it does not prevent phosgene gas production during reaction. To limit the toxicity risks associated with remaining phosgene, the latter can be neutralized with an aqueous solution of sodium hydroxide.

One last method that looks very attractive, since it is using mild conditions and is phosgene free, is the reaction of aniline compounds with di-*ter*-butyl dicarbonate (Boc_2O) in the presence of a stoichiometric amount of 4-dimethylaminopyridine (DMAP) in an inert solvent (dichloromethane, acetonitrile, ethyl acetate, tetrahydrofuran, toluene) and at room temperature (Scheme 19) [181]. The main drawback of this reaction is the fact that it does not work with highly reactive compounds such as alkyl amines since the resulting isocyanate reacts almost instantaneously with the unconverted amine, yielding ureas.

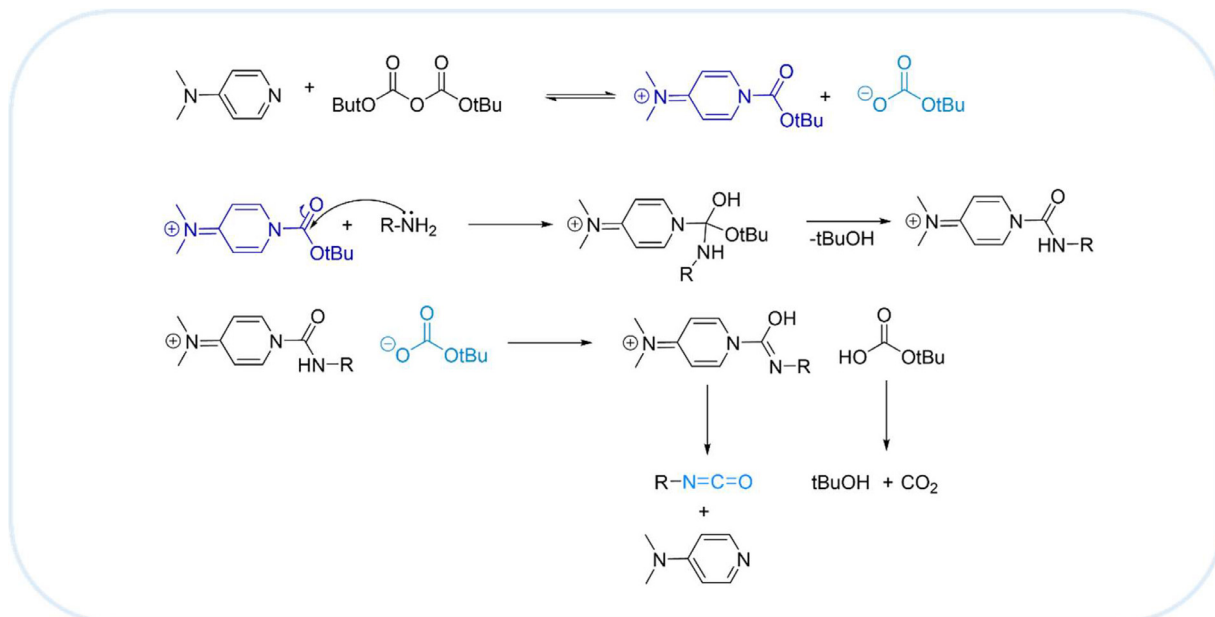
Although these synthetic pathways old promise because they lead to the production of isocyanate without the use of phosgene, the phosgene synthetic pathway is well mastered by indus-



Scheme 17. Lossen rearrangement [179].



Scheme 18. Triphosgenation reaction [180].

Scheme 19. Reaction of Ph-NH₂ with Boc₂O [181].

try and the cost of this route is much less expensive than the cost of the routes describe here. In addition, most of these alternative pathways start also from harmful raw materials, such as triphosgene, azides or carbon monoxide. It can thus be assumed that the phosgene-route towards isocyanates will not be abandoned soon at industrial level. Nevertheless, to diminish the toxicity of isocyanates over their life cycle (synthesis and handling), other strategies have proven effective. In particular, the use of NCO-terminated prepolymers that are viscous or solid compounds allows to reduce isocyanate toxicity by lowering their reactivity (hindered NCO function) and vaporization pressure. Scheme 20 shows the different non-phosgene routes to synthesize isocyanates.

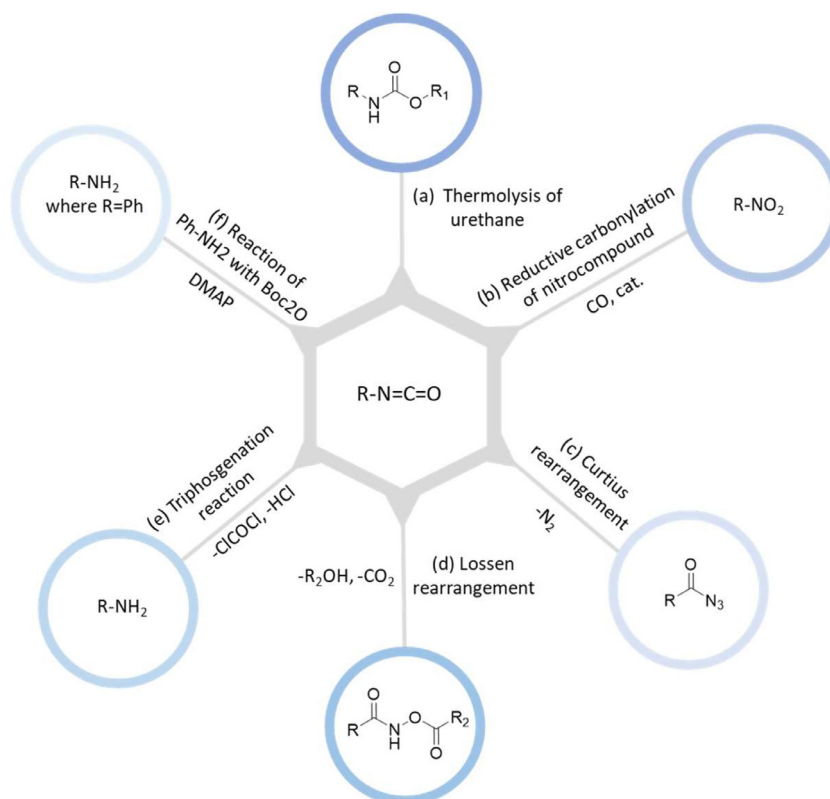
4.2. Bio-based isocyanates

As bio-based polyols, bio-based isocyanates represent an interesting solution to lower the carbon footprint of isocyanates. Numerous chemical companies are thus interested in developing and marketing bio-based di- or poly-isocyanates monomers for PU industry. Among them, Alfa Aesar sells a diisocyanate synthesized from the ethyl-ester of the essential L-lysine amino acid, namely L-Lysine ethyl-ester diisocyanate (LDI, represented in Fig. 8). The bio-based carbon content of this monomer could reach 80 % if the ethanol used in the esterification step was bio-based. Besides its natural origin, this diisocyanate also allows to produce fully

biodegradable PU materials, solving environmental issues associated with PUs' end of life [126,182,183]. Nevertheless, the main drawback of this product is its high cost, which limits its uses to PUs dedicated to biomedical purposes.

Vencorex®, a French company, manufactures a difunctional isocyanate monomer known as Tolonate™ X FLO 100. The bio-based carbon content of this molecule is around 32 % according to ASTM D6866. Tolonate™ X FLO 100 is composed of an hexamethylene isocyanate allophanate with PEG as side chain and the bio-based moiety is a palmitic acid unit [184,185]. This product presents a very low viscosity and can be used as a reactive monomer or as a good diluent in PU formulations.

Mitsui Chemicals® and Covestro® both propose an isocyanurate of pentamethylene diisocyanate (PDI) with a bio-based content around 68-71 % since PDI is derived from glucose. Covestro® markets this PDI-based isocyanurate under the trade name of Desmodur® eco N7300. This product exhibits a high viscosity around 9,500 mPa.s at 20°C, making its handling quite complicated [186]. The high viscosity of Desmodur® eco N7300 is probably due to the lack of control during trimerization as explained in the previous section. Mitsui Chemical® proposes two different grades of isocyanurate-based PDI under the trade name Stabio™, with two different viscosities. While Stabio D-370N shows a moderate viscosity around 2,000 mPa.s at 20°C with a bio-based content of 70 %, the Stabio D-376N exhibits a lower viscosity around 900 mPa.s



Scheme 20. Non-phosgene routes to isocyanate synthesis.

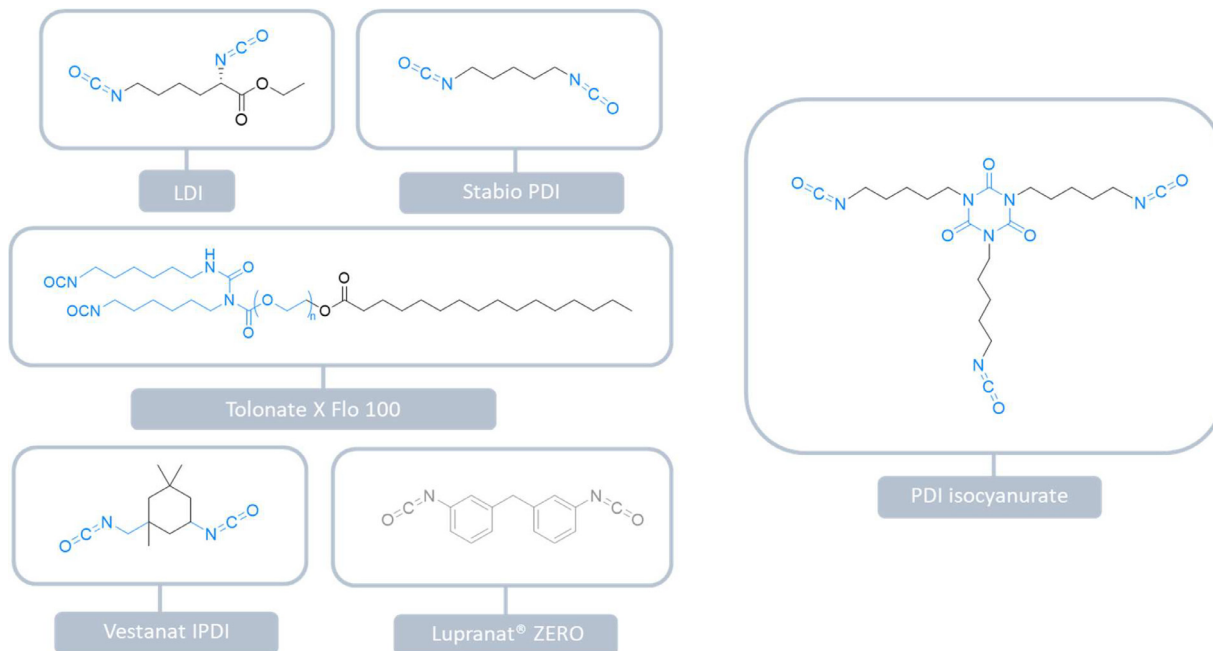
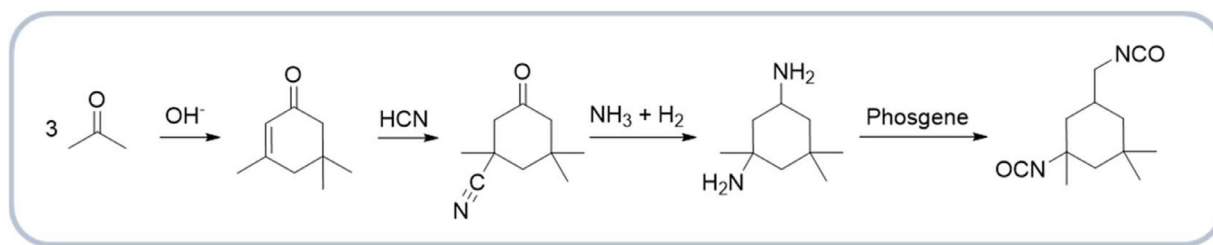


Fig. 8. Ideal structures of commercially available bio-based isocyanate compounds. Black moieties come from petro-based raw materials, blue moieties from bio-based raw materials. No indications are given regarding the raw materials used for Lupranat® Zero.

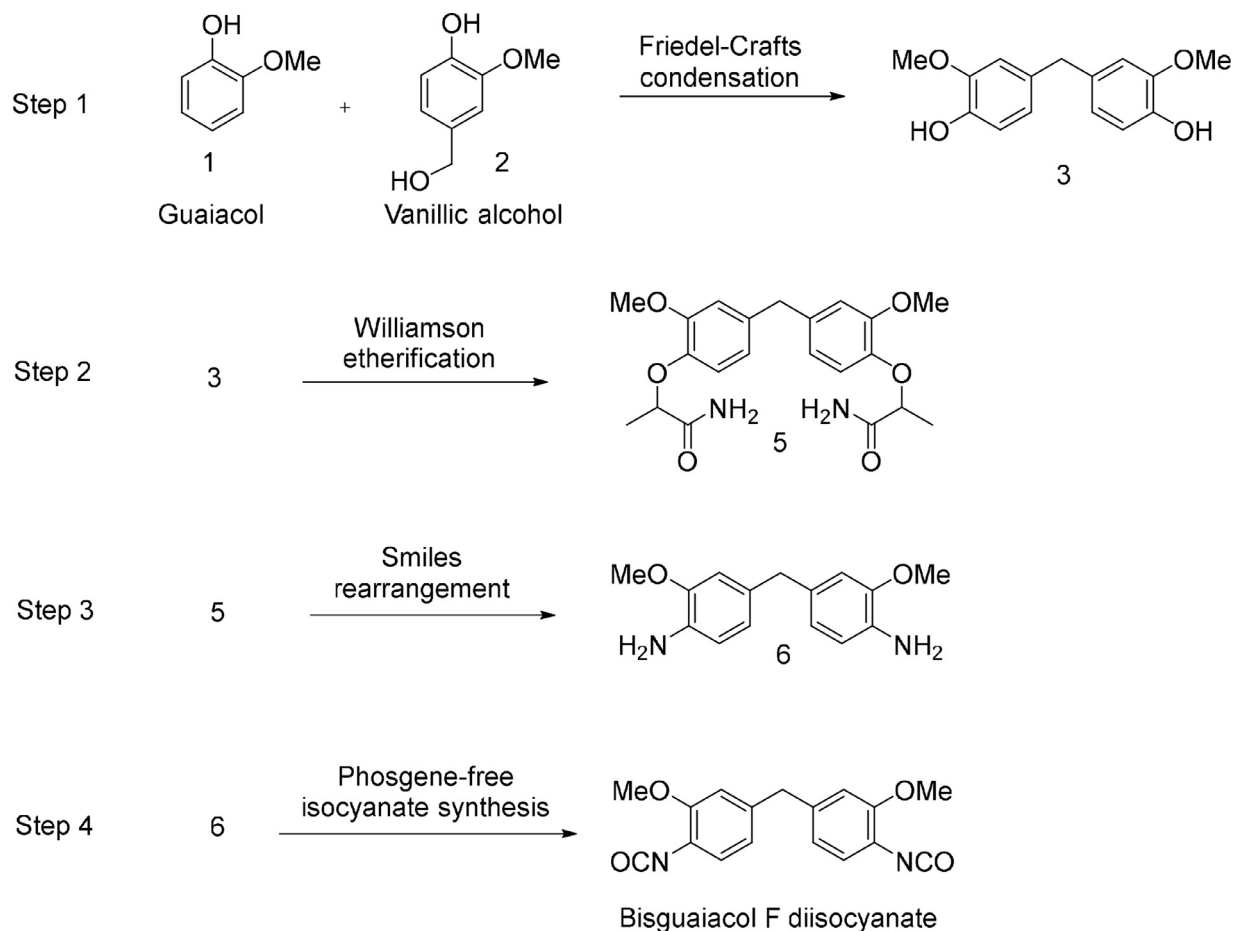
a 20°C with a bio-based content of 68 % [187]. Mitsui Chemicals® also markets PDI monomer with a calculated bio-based content of 71 %.

Very recently, Evonik launched sustainable IPDI made from 100 % renewable acetone under the tradename VESTANAT® IPDI eCO [188]. IPDI is basically produced through a sequence of chemical reactions where the raw material required is acetone, as de-

picted in Scheme 21. Acetone is converted into isophorone, then isophorone diamine and to finish into isophorone diisocyanate. Evonik policy try to identify the factors that have impacts on the total global warming potential (GWP) of their products. They found that acetone is responsible for 30 % of the GWP of petrochemical based IPDI. That is the reason why Evonik decided to work with more environmentally friendly acetone to synthesize an



Scheme 21. IPDI synthesis [189].



Scheme 22. Chemical approach for the synthesis of Bisguaiacol F diisocyanate.

ecofriendly IPDI. Renewable acetone can come from three different sources: feedstocks from agricultural industry like corn or cotton, feedstocks from vegetable-based wastes or residues like cooking oils or forestry residues and feedstocks using recycled carbon from plastic wastes. They ensure that GWP of IPDI can be reduced of 40 % when sustainable acetone is used and displays 75 % of bio-based carbons.

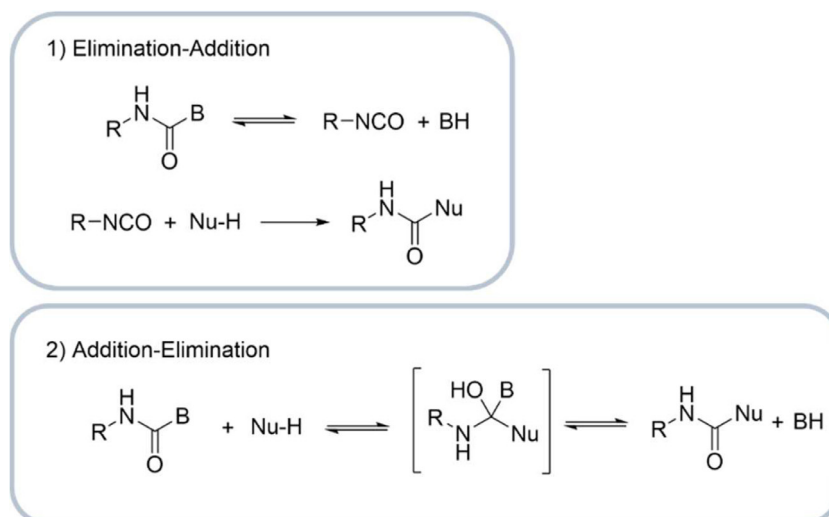
In the same initiative, BASF introduced, in the early part of 2022, Lupranat® ZERO [190]. This new product of their portfolio is described as a zero emission and renewable MDI. BASF did not give clarification about the renewable origin of the raw material used but promised to their customers that its use will reduce their CO₂ footprint. Besides, Covestro® is working on 100 % bio-based aniline to produce MDI by using microorganisms as catalysts to force the conversion of sugar into this precursor. This work is still ongoing but promises the release of bio-based MDI by Covestro®.

At academic level, Lemouzy and Delavarde [191] recently described a 4-step phosgene-free and transition-metal free synthesis

of a bio-based surrogate to MDI, namely Bisguaiacol F diisocyanate from lignin-derived raw materials (Scheme 22). Their work showed promising results proving that it is possible to propose a sustainable alternative to the synthesis of MDI monomer.

Finally, some articles mention the existence of a bio-based diisocyanate from dimer fatty acid commercialized by BASF. However, to the best of our knowledge, it has been impossible to get this raw material.

In conjunction with bio-based polyols, bio-based isocyanates offer the opportunity to develop almost fully bio-based PUs. This strategy has been first described by Morales-Cerrada *et al.* [184] who worked especially on developing PU thermosets by one pot and two-step methods. For the one-pot method, formulations composed of castor oil and a bio-based polyisocyanate compound, LDI (named L1 formulation), Tolonate™ X FLO 100 (named T1 formulation) or Desmodur eco N7300 (named D1 formulation) were prepared. After curing, the resulting PU materials displayed a *T_g* roughly like other castor oil-based formulations, *i.e.* -26.8°C for L1, -



Scheme 23. Generalized reactions systems for the deblocking reaction of blocked isocyanate, where BH is the blocking agent and Nu-H an active hydrogen compound such as alcohols and amines [197].

38.4°C for T1 and -31.7°C for D1. Regarding two-steps formulations, they first synthesized prepolymers using bio-based polypropanediol and either LDI (named L2 formulation), Tolonate™ X FLO 100 (named T2 formulation) or Desmodur® eco N7300 (named D2 formulation). In the second step, glycerol was used as chain extender to provide PU thermosets. The T_g values of materials resulting from L2, T2, D2 exhibited different behaviors depending on the functionality of isocyanate. Difunctional isocyanates (L2 and T2) gave PU thermosets with low T_g values, quite similar to castor-oil based formulations (*i.e.* -11.7°C and -40.7°C). However, the trifunctional isocyanurate based PU (D2) displayed a T_g value at +21.2°C.

Quienne *et al.* [192] also worked with Tolonate™ X FLO 100 and LDI to design partially bio-based PU foams. They showed that LDI-based formulations foamed at room temperature while Tolonate-based formulations must be heated to perform a complete foaming, proving that LDI seems to have a higher reactivity than Tolonate™ X FLO 100. Moreover, LDI-based foams exhibit higher T_g values (12°C and 46°C) than Tolonate-based ones (-29°C and -26°C) which is logical in regard to the structure of the two bio-based isocyanates. Interestingly, the obtained foams could be reshaped up to 5 times by compression molding thanks to the use of DBTDL as a transcarbamoylation catalyst (see Section 7.2).

Some other researchers [193–196] worked with these commercially available bio-based polyisocyanates to formulate PU materials. In each case, these products showed really promising results, which is announcing a big future for bio-based PU industry.

To resume, industries show a growing interest in bio-based polyfunctional isocyanates to give a more sustainable future to PU market. Two different strategies seem to be followed by industrial companies: i) the drop-in route which consists in synthesizing existing petroleum-based polyisocyanates but in a bio-based version, and ii) the other route which consists in synthesizing structurally new bio-based polyisocyanates with a lower toxicity. Even if still at early stages, these outcomes promise the rollout of new products in the following years.

4.3. Blocked isocyanates

A blocked isocyanate is an isocyanate that has been reacted with a compound containing an active hydrogen to prevent its reaction at room temperature. The unblocking reaction is dependent on the reaction temperature, the structure of the blocking component, the presence of a catalyst and the effect of the sol-

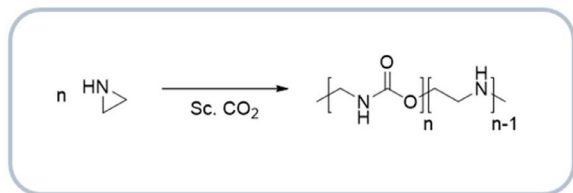
vent [197]. Aliphatic and aromatic isocyanates can be blocked by a variety of compounds including alcohols, phenols, oximes, lactams, amines, malonic esters, etc. There are two different accepted mechanisms to explain the deblocking reaction of a blocked isocyanate: elimination-addition or addition-elimination, as illustrated in Scheme 23. Once an isocyanate is unlocked, it can be used as a simple isocyanate to form PU materials.

At first, blocked isocyanates were developed to create one-component “baking enamel” type of coating systems that are used for coil coatings, powder coatings, electrodeposition coatings, and some other metal finishing applications where the coatings are cured at a high temperature, 160°C or higher. Nevertheless, blocked isocyanates also allow reducing isocyanate toxicity by hindering the isocyanate function. It should be noted, however, that most companies using blocked isocyanates will have afterburners in their exhaust systems to incinerate the released blocking agents, generating VOCs or CO₂. This technology should thus not be employed to lower the environmental impact of PUs.

One of the most used blocking agents is phenol. It was demonstrated that urethanes formed from the reaction of an isocyanate and a phenol will thermally dissociate more easily than urethanes formed from the reaction of an isocyanate with an alcohol [198]. However, to avoid toxic phenol release when the blocked isocyanate is reacting, safer blocking agents can be used, like vanillin for example [199].

The use of blocked isocyanates can reduce, or eliminate, the toxic hazards related to the nature of isocyanates compounds. Indeed, the blocked isocyanate is an inert and non-hazardous material at room temperature. Moreover, for certain applications, such as powder coatings, coil coatings or cationic electrodeposition coatings, blocked isocyanates are used to provide one-pot coatings [200]. These one-component formulations are containing hydroxyl-ended compounds and blocked isocyanates. They are particularly useful for waterborne PU coatings (see Section 6.2 on waterborne polyurethanes) since the isocyanate would react with water instead of polyols [201–203].

As mentioned previously, besides lowering their reactivity, it is also possible to limit the isocyanate toxicity by limiting their diffusivity or lowering their vapor pressure, for example by targeting compounds that present less risks such as isocyanate-terminated prepolymers. However, for applications where isocyanate residues are prohibited (such as biomedical, food industry or detergent industry), other strategies to obtain polyurethanes without using iso-



Scheme 24. Copolymerization of aziridine with super critical carbon dioxide [205].

cyanates have been developed, such as the cyclocarbonate aminolysis leading to the formation of polyhydroxyurethanes (PHU). These synthetic pathways to NIPUs are the topic of the next section.

5. Different routes to isocyanate-free polyurethanes

Due to the isocyanate toxicity, alternative reactions are investigated to synthesize polymers with the same properties than conventional PUs but without using isocyanates as starting building blocks. NIPUs were born in this context [21]. Nowadays, there are several synthetic pathways to obtain materials containing carbamate linkage without the use of isocyanates. Among the different synthesis pathways, the aminolysis of cyclocarbonates is certainly the most studied. Nevertheless, the copolymerization of aziridine with carbon dioxide or the ring-opening polymerization of cyclic carbamates also represent interesting alternatives. Indeed, some of these routes are more studied than others depending on several factors such as the toxicity of their precursors, the synthesis conditions or/and the relative reactivity of chemicals.

5.1. Copolymerization of aziridine with carbon dioxide

Inspired by Inoue *et al.* [137] who achieved the production of a polycarbonate from carbon dioxide and epoxide in 1969, several research groups synthesized PUs from carbon dioxide and aziridine during the 70's. For instance, Kuran *et al.* [204], carried out the synthesis of PU oligomers ($500 \text{ g}\cdot\text{mol}^{-1}$) in the presence of an organozinc catalyst. These new PUs were synthesized without the use of either phosgene or isocyanate. However, this synthetic pathway yielded PUs with a low carbamate linkage content (30%) since the major reaction was the homopolymerization of aziridine [205], see Scheme 24. In order to tackle this issue and increase the percentage of carbamate linkages, supercritical carbon dioxide (scCO_2) can be used as a reactant, hence allowing the catalyst free synthesis of poly(urethane – amine) (Scheme 24). At 22 MPa CO_2 pressure, polymers with high content of carbamate moieties were obtained (62 %) [206]. In their report, Ihata *et al.* [206] did not dis-

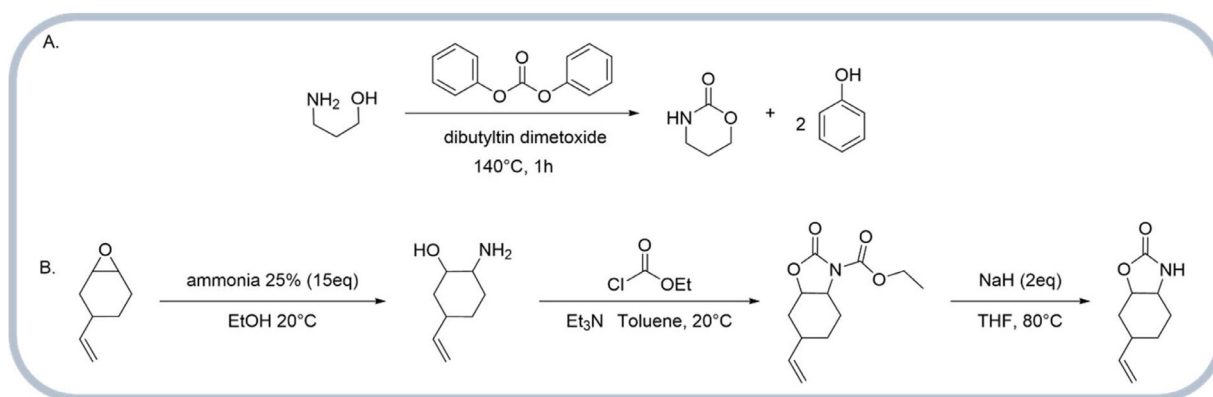
cussed the thermal and mechanical properties of as formed PUs; only elementary analysis being performed. It seems that these syntheses were carried out just to prove the possibility to obtain PUs materials with this method.

In the last few years, very few materials were synthesized using the aziridine copolymerization because of its multiple disadvantages. First, under supercritical conditions, the carbamate content increases from 30 % to 60 %: a yield that still needs improvements. Secondly, the amine residue can affect the properties of the materials. The major disadvantage with these NIPUs, which limits their use, is the toxicity of aziridines that are classified as CMR (oral $\text{LD}_{50\text{-rat}}$ (ethyleneimine) = $15 \text{ mg}\cdot\text{kg}^{-1}$, oral $\text{LD}_{50\text{-rat}}$ (TDI) = $4,000/6,000 \text{ mg}\cdot\text{kg}^{-1}$, and $75 \text{ mg}\cdot\text{kg}^{-1}$ for the corresponding amine).

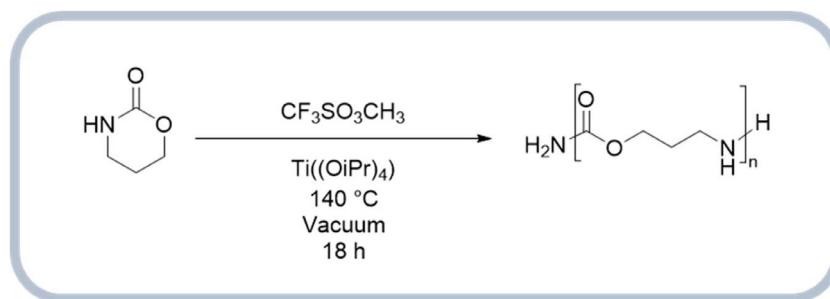
5.2. Ring-opening-polymerization of cyclic carbamate

According to Zhang *et al.* [207], the ROP of a cyclic carbamate offers more advantages than other common routes to obtain the corresponding polyurethane. In fact, it bypasses the low reactivity of the cyclocarbonate-amine reaction (discussed in the following part 5.3) and avoids the use of toxic reagents. Despite the low reactivity of the monomers, the ROP exhibits atom economy, waste reduction and low energy consumption. Following this pathway, NIPUs can be obtained with a high yield and under mild condition after monomer's synthesis. For instance, the monomer synthesis can be achieved in either a one-step reaction with diphenylcarbonate and 3-aminopropan-1-ol as starting materials, as seen in Scheme 25-A, or in several steps using ethyl chloroformate and β -hydroxylamine compounds (Scheme 25-B). However, these syntheses rely on a hazardous reagent (ethyl chloroformate, oral $\text{LD}_{50\text{-rat}}$ is 505 mg/kg , phosgene based) or catalyst (dibutyltin dimethoxide, oral $\text{LD}_{50\text{-rat}}$ $100 \text{ mg}\cdot\text{kg}^{-1}$) and release harmful byproducts such as phenol (CMR, oral $\text{LD}_{50\text{-rat}}$ = $317 \text{ mg}\cdot\text{kg}^{-1}$).

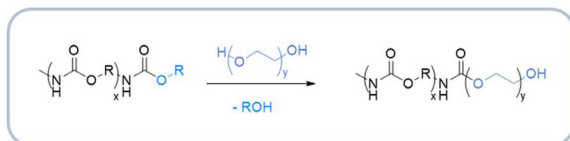
After these reactions, the cyclic carbamate can be opened with a cationic or anionic initiator, both with good yields [207]. As depicted in Scheme 26, Neffgen *et al.* [208], showed that trimethylene urethane, which is the main reaction product from Scheme 25-A, can be polymerized by cationic ring-opening polymerization catalyzed by methyl trifluoromethanesulfonate. They demonstrated that with titanium tetraisopropoxide ($\text{Ti}(\text{OiPr})_4$) at 140°C under vacuum for 18 h, it is also possible to depolymerize the formed PUs by ring closure. However, under the same conditions, the polymerization of 2,2-dimethyltrimethylene urethane, which is a trimethylene urethane with two methyl groups in meta position, could not be achieved. Zhang *et al.* [207] reported that 5 membered aliphatic cyclic urethanes can also be polymerized by anionic ROP with trium(III) isopropoxide.



Scheme 25. Different ways of cyclic carbamate synthesis A. One step reaction, B. Several steps.



Scheme 26. Polymerization condition of trimethylene urethane and depolymerization condition of its linear urethane counterpart.



Scheme 27. Synthesis of PUs by transurethanization of PU oligomers with polyethylene glycol.

To summarize, the ROP of cyclic carbamates although interesting possesses several drawbacks that are still to overcome. For instance, several syntheses steps are required to obtain the final PU, which is time consuming and limit the atom economy. Additionally, harmful reagents are used and CMR by-products are formed such as phenol. Moreover, the variety of PU that can be synthesized following this route is limited to the cyclic carbamates that can be synthesized. For all these reasons, the ROP of the cyclic carbamates is studied by only a few teams around the world, such as Haba *et al.* [209], and Zhang *et al.* [207].

5.3. Transurethanisation

Transurethanization or transcarbamoylation is another way to obtain the carbamate linkage without using phosgene or isocyanate. As seen in Scheme 27, an alcohol reacts with an existing urethane, leading to a new urethane moiety [210]. The side product of this condensation is a low molecular mass alcohol that can be removed from the reaction media by distillation to push the reaction forward. However, a major drawback of this reaction is the fact that, even if the product is a NIPU, the starting carbamate usually comes from an isocyanate synthesized with phosgene. To increase the sustainability of this synthesis, non-isocyanate-based carbamates can be involved. These carbamates can be formed *via* different synthetic pathways such as the cyclic carbonate-amine reaction and the reaction of DMC with a diamine [211]. For instance, to obtain a NIPU by transurethanization, Kébir *et al.* [212] first synthesized a NIPU from the well-known aminolysis way using DMC and a diamine (1,6-hexadiazine, 1,10-decanediamine and Priamine 1074). Then, they used different molar masses PEG to yield a soft segment in the PU structure. Catalyzed by triazabicycloundecene (TBD), this reaction was performed at 160°C to obtain polymers with low T_g (-49°C to -1°C), depending on the molar mass of the PEG employed. As compared to their PU analogues, these NIPU exhibited better thermal stabilities [213].

Until now, this method is certainly one of the most sustainable reported, considering that the DMC and the amine can be bio-based and nontoxic. The minor drawbacks that can be noted are the high temperature required to perform the reaction, the need for a catalyst and the generation of a low molar mass alcohol. This reaction also represents a convenient method to recycle PUs when mono alcohols are employed in place of diols [214].

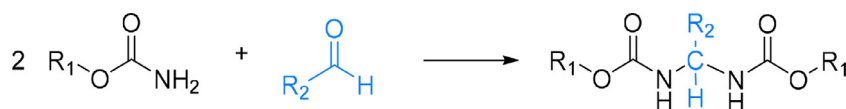
5.4. Carbamate/aldehyde reaction (CA)

In the 19th century, Bischoff [215] initially reported the carbamate/aldehyde reaction, inspired by Roth's earlier work [216]. Despite, this method is not widely adopted for synthesizing NIPU, it has recently attracted more attention, particularly for coating preparation [217–219]. This method involves the reaction between a primary carbamate, an aldehyde and an acidic catalyst, resulting in the formation of two urethane groups attached to the same carbon atom, as illustrated Scheme 28. This implies that a single aldehyde can react with two carbamates, a quite distinctive feature of the reaction.

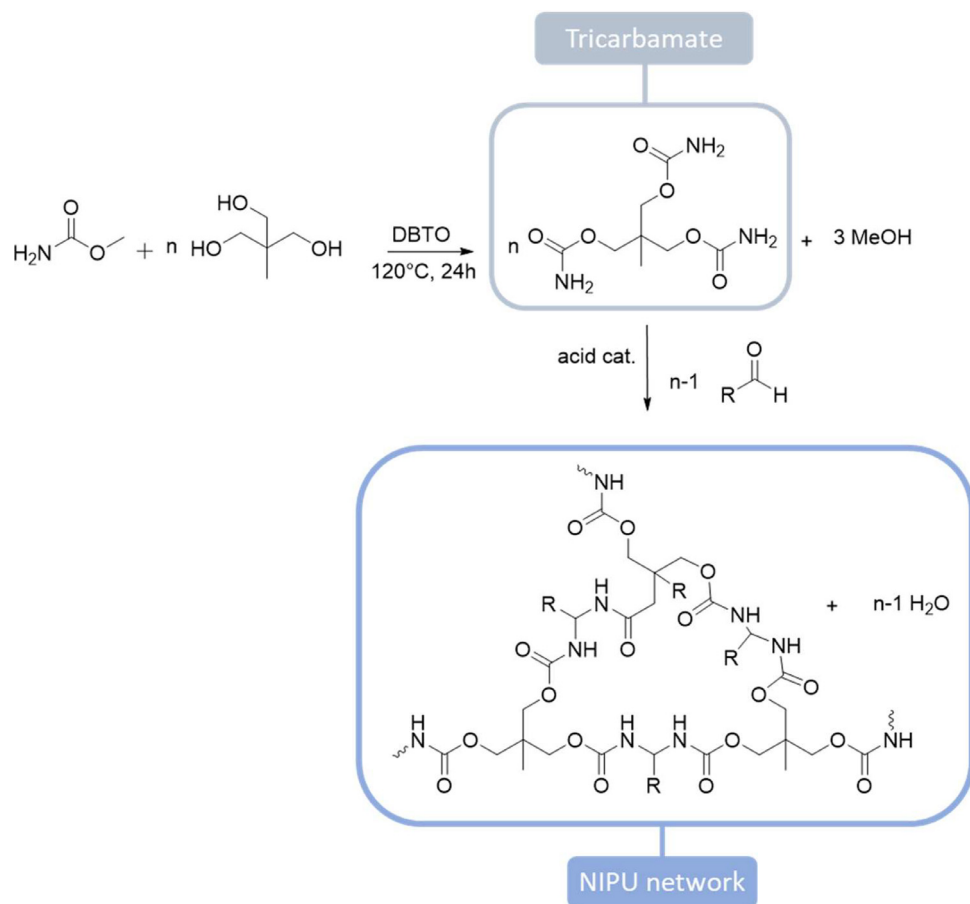
The ability to prevent the production of VOCs makes this reaction particularly interesting, as the only byproduct obtained is water.

From industrial standpoint, Dow Global technologies LLC filled multiple patents related to this reaction [220–223]. They reported that the synthesis can be carried out at relatively low temperatures ranging from 0 to 80°C. At room temperature, it takes approximately a week for the reaction to reach complete curing, whereas at 60°C, only half an hour is required. David Gerard *et al.* [217] brought innovation to Dow's existing patents by working to enhance the sustainability of carbamate/aldehyde reaction through the use of monoaldehydes since they are less toxic than polyaldehydes. More specifically, they decided to use commercially available bio-based aldehydes, such as 5-methyl furfural and vanillin. By reacting a tris-carbamate, obtained by transurethanisation between trimethylolpropane and methylcarbamate with vanillin at 120°C, as displayed in Scheme 29, they were thus able to synthesize a PU thermoset having a T_g of 65°C and a gel fraction of 82%. Similarly, several bio-based coatings were prepared by Silbert *et al.* [219] by reacting soybean oil-derived polycarbamate with 1,4-cyclohexanedicarboxaldehyde or 2,5-diformylfuran. A temperature of 120°C was also found necessary to obtain cross-linked materials in reasonable times (2 h at 120°C vs 180 days at RT).

The carbamate-aldehyde reaction is an underappreciated process that holds significant potential for the synthesis of NIPU.



Scheme 28. Carbamate/aldehyde reaction.



Scheme 29. Synthesis of NIPU network from trimethylpropane, methylcarbamate and an aldehyde.

While avoiding the generation of toxic byproducts or VOCs, this reaction also offers the opportunity to produce PU with high bio-based content since many bio-based aldehyde compounds are available on the market and bio-based polycarbamate can be easily obtained from biobased polyols and methylcarbamate. Nevertheless, further research is required to optimize the current synthesis conditions as to lower reaction times and temperatures and to attain higher yields.

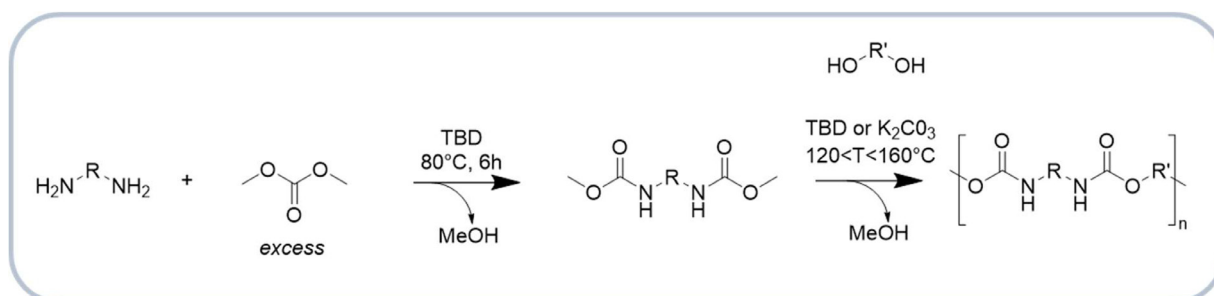
5.5. Aminolysis of carbonates

5.5.1. Linear carbonate

To avoid the use of isocyanates, carbamate linkages can also be obtained by aminolysis of alkylcarbonate, as seen in [Scheme 30](#). Most often, dimethylcarbonate (DMC) is employed as starting compound since it is liquid and upon aminolysis, it releases only

methanol that can be easily removed from the reaction media. The reaction is usually conducted with an excess of carbonate in order to solubilize the amine and in the presence of a catalyst. Initially, metallic-based catalysts such as scandium(III) triflate or lead(II) nitrate were used. However, these catalysts tend to be replaced by organic ones like TBD or tetrabutylammonium bromide (TBAB) [21]. Interestingly, aminolysis of linear carbonates can be performed without solvent and without catalyst, making this reaction eco-friendlier.

This technique allows to obtain dicarbamate monomers that can be polymerized via transesterification in presence of diols to form TPUs [21,224]. Duval *et al.* [213] used this methodology to obtain NIPUs from several renewable diamines and diols such as 1,6-diaminohexane or priamine and butandiol or diol prepared from methyl ricinoleate, respectively. NIPUs with M_n ranging between 3,000 and 14,000 $\text{g}\cdot\text{mol}^{-1}$ were thus obtained. Among the



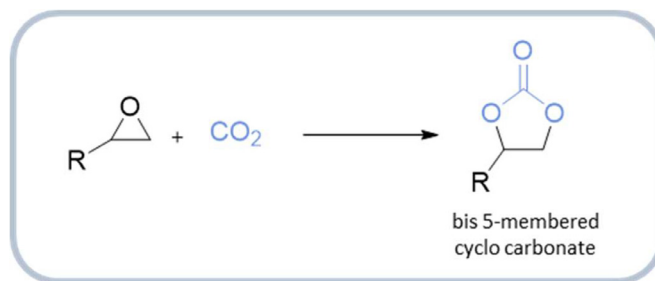
Scheme 30. Aminolysis of dimethylcarbonate to produce a dicarbamate subsequently employed for the synthesis of a TPU.

two catalysts (TBD or K_2CO_3) employed for the transurethanization reaction, K_2CO_3 proved the most effective by allowing higher reaction temperatures and thus the production of NIPU with higher \bar{M}_n . Similarly, Wolosz *et al.* [225] synthesized NIPUs in bulk from dimethylcarbonate and aliphatic or aromatic diamines for the first step, and 1,5-pentandiol or 1,6-hexandiol for the second step of the reaction with zinc acetate as catalyst of transurethanization. The obtained NIPUs displayed molar masses in the same range as those reported by Duval *et al.*, i.e. of 7,000-18,000 $g \cdot mol^{-1}$. Besides, their mechanical properties were found similar to PUs of the same structure obtained by the alcohol-isocyanate route. Taking advantage of the fact that NIPUs obtained following this strategy are often of low molar mass, Boisaubert and his team [226] synthesized NIPUs oligomers with hydroxyl chain-ends that were further converted into acrylate moieties. By photo-crosslinking, these NIPU-acrylates (NIPUAs) in the presence of reactive diluents they were able to prepare coatings exhibiting thermal and mechanical properties in line with those of the flexible PUs currently developed on the market: $E=2.6-9.2$ MPa and elongation at break from to 20 to 520 %.

Despite research efforts on NIPUs synthesis to increase molar masses and thus mechanical properties, NIPUs usually display lower mechanical properties than conventional PUs. As reported by Shen *et al.* [227] this feature relies on crystallization behavior and morphology of NIPUs as compared to their isocyanate-based analogues. Studying NIPUs based on bis-1,6-hexamethylencarbamate, 1,6-hexandiol, and polytetramethylene ether glycol, and their PU analogues based on 1,6-hexamethylenediisocyanate they showed that, due to a higher content of urea groups in NIPUs, the thermal and mechanical properties are lower to PUs counterparts. Indeed, during the transurethanization process, terminal hydroxyls react with carbamate group leading to a terminal amine and a terminal carbamate. The amine group consecutively reacts with another carbamate bond to form urea group. The strength of hydrogen bonding between hard segments and the crystallinity of the hard phases are thus lower than those of PUs. Nevertheless, it should be noted that when the formation of urea bonds can be avoided, as during the synthesis of NIPUs from priamine reported by Wolosz *et al.* [228], NIPUs with high \bar{M}_n and with good mechanical properties, similar to their PU analogues, can be obtained. These last results highlight the fact that research should focus on finding transurethanization catalysts that favor the formation of carbamate bonds over the formation of urea.

5.5.2. Cyclic carbonate

Patented in 1954 by Groszos *et al.* [229], the synthesis of PHU by aminolysis of cyclocarbonates is a highly promising polymerization method, which involves, most of the time, a bis-5-membered cyclic carbonate and a diamine. Knowing that many reviews have focused on the synthesis of NIPUs by aminolysis of cyclocarbonates [21,23,24,35,224,230-234], this part will mainly focus on 5-membered cyclo-carbonate (5CC) because they are CO_2 -based and can be bio-based.



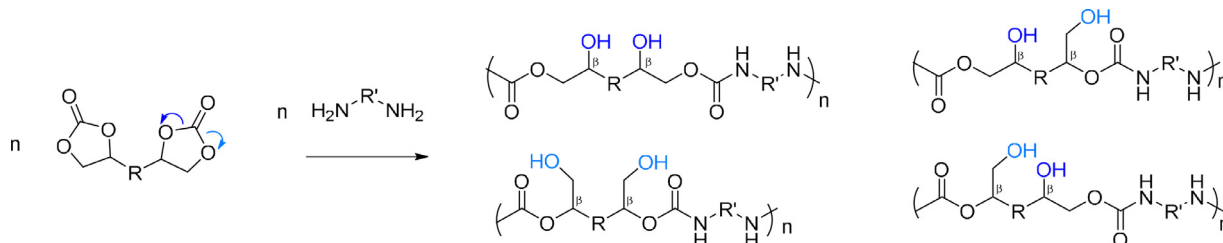
Scheme 31. Synthesis of cyclic carbonate by carbonatation of an epoxy ring.

5CC are commonly produced from the corresponding epoxide and carbon dioxide at high temperature and pressure in presence of an appropriate catalyst as depicted in [Scheme 31](#) [23,235].

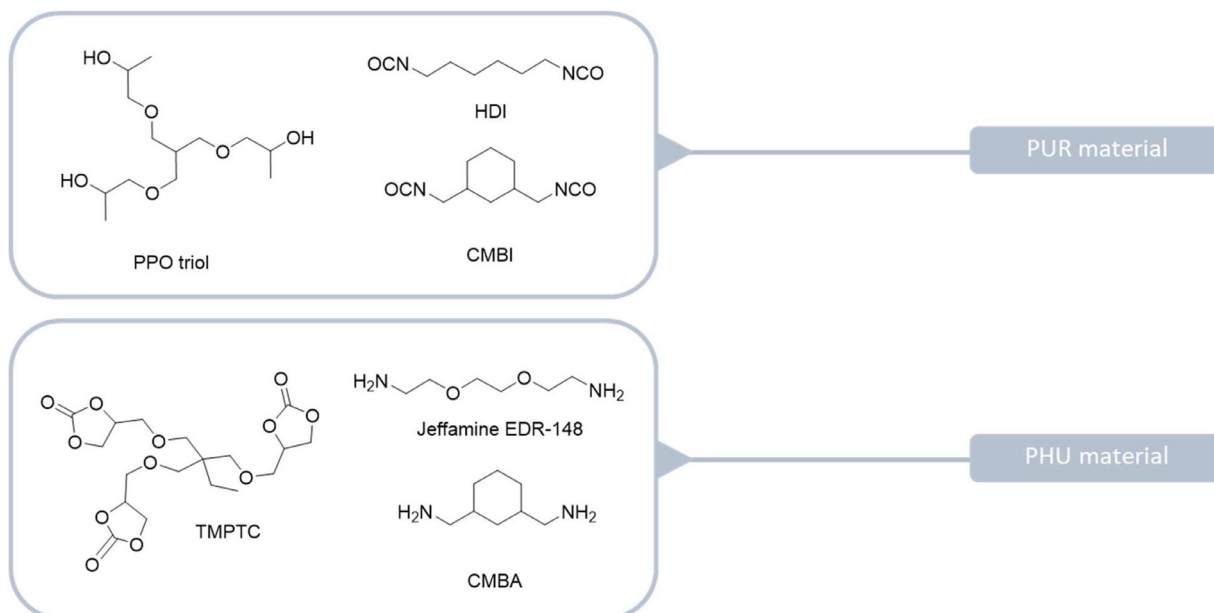
Nevertheless, Büttner *et al.* [236] worked on more efficient catalytic systems to allow the reaction to take place at temperatures $<100^\circ C$ and/or CO_2 pressures inferior to 0.1 MPa. They investigated organocatalysts such as ammonium and imidazolium salts, offering a modular synthesis with easy modification and optimization of the catalyst structure.

Regarding PHUs synthesis, the reaction is slow at room temperature due to the relatively stable nature of cyclic carbonates as compared to their epoxide equivalents. The resulting polymer is so called because additionally to the carbamate function, a hydroxyl group is generated. As seen in [Scheme 32](#), the reaction between bis-5CC and diamines leads to the formation of linear PHUs with primary and secondary alcohols. According to Kathalewar *et al.* [23], the formation of PHUs containing secondary alcohol is favored compared to the ones with primary alcohol (ratio 80:20 found for 5CC with benzylamine or hexylamine) [237].

These pending OH groups bring numerous advantages to PHUs over regular PUs. For example, they can be used for post functionalization [22,237]. Besides, numerous intra- and intermolecular hydrogen bonds are formed with the urethane moiety, resulting in higher mechanical strengths and improved chemical resistance to non-polar solvents than PUs [22]. Moreover, the absence of unstable biuret and allophanate units seems to be responsible for increased thermal stability and chemical resistance (1.5 to 2 times greater than materials that possess similar structure with such hydrogen bonds [238]) to non-polar solvents [232]. Due to this ability to form hydrogen bonds, PHU can be blended with hydrophilic biopolymers such as starch [239], decreasing the Young Modulus and tension at break. It thus opens new possibilities to use these materials for biomedical devices, wound dressing, and food packaging. For example, Lambeth and Rivzi [240] prepared a hybrid epoxy-PHU blend, with a decrease in the rubbery modulus compared with virgin epoxy sample, which was attributed to a decrease in the crosslink density. However, the T_g was shifted to higher values, likely due to the hydrogen bondings, limiting the segmental motion of the polymer chains.



Scheme 32. Synthesis of PHU from bis 5CC and diamines; the 4 possible structures of the resulting PHU are represented.



Scheme 33. Monomers employed for the synthesis of the first 100% PHU adhesive structure and its PU counterpart [245].

The carbonate-amine chemistry provides PUs with promising features through a safer route. The toxicity of amine and carbonate precursors is indeed very mild as compared to isocyanates. On the other hand, reagents are non-moisture sensitive contrarily to isocyanates. No caution is needed to store them and the formation of side products such as isocyanurates during storage is eliminated.

Researchers are also trying to develop these precursors starting from bio-based synthons [21] (e.g. vegetable oils, terpenes, sugars for the CC and fatty diacids for the diamines). For example, epoxidized soybean oil can be used as multifunctional 5CC precursor to synthesize cross-linked NIPU [224].

In literature [24,82,241,242], it has been demonstrated that bio-based PHUs consistently play a role in decreasing the carbon footprint of NIPUs. Additionally, the cyclic carbonate-amine reaction is recognized for its 100 % atom efficiency. Among the various types of NIPUs, PHUs derived from renewable sources have received significant attention from research groups such as Caillol, Cramail, and Detrembleur, who have extensively investigated these systems.

Like polyurethanes, PHUs exhibit adhesion characteristics due to their dense network of hydrogen bonding. They can adhere to many surfaces such as wood, glass or aluminum [243]. After the work of Leitsch who synthesized an adhesive based on PU/PHU [244], Cornille *et al.* [245] pioneered the first 100 % based PHU adhesive. In this work, the adhesion of PHU synthesized with trimethylol propane triscarbonate (TMPTC) and Jeffamine EDR-148 or 1,3-cyclohexanebis(methylamine) (CBMA) was compared to the adhesion of the analogous PU made with poly(propylene oxide) triol (PPO triol) and HDI or cyclohexane 1,3-diisocyanate (Scheme 33). This study concluded that the adherence on aluminum of PU and PHU are close. However, the adhesive properties of PHU largely surpass the one of PU on wood. This can be explained by the presence of free hydroxyl groups along the PHU chain, which allows the material to do additional hydrogen bonding with the polysaccharides contained in the wood.

Through the reaction between polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyfunctional amines bearing primary amino groups, a cross-linked polymer can be generated if at least one of the reagents possesses a functionality higher than two [232]. Since NIPUs are obtained without using the toxic and harmful isocyanates, the synthesis process is relatively safe for both hu-

mans and environment, compared to the production of the conventional PUs.

Sukumaran *et al.* [246] also showed a green synthetic route to obtain hybrid PHUs with thermo-reversible adhesion features. They synthesized a hybrid PHU by copolymerizing an aromatic cyclic carbonate (BACC) with aliphatic cyclic carbonates (CYCC) monomers in different molar ratios with polyether amine-400 (PEA400) (Fig. 9). The aromatic content in hybrid PHU enhanced the T_g from 5 to 18°C.

The interaction between isocyanate and water during the formation and storage of moisture-curing PU coatings poses challenges [247]. Indeed, the system needs to be carefully isolated from water until it is applied to the surface to be coated. Otherwise, the polyfunctional isocyanates components and water would undergo cross-linking, forming urea and releasing CO₂, resulting in a hardened unusable product. One of the solutions found to overcome this problem, besides the use of blocked isocyanates, is to add moisture scavenging compounds such as molecular sieves or latent curing agent [247]. On the contrary, due to their unique molecular composition, NIPUs are transformed into a material with practically no pores, meaning that, once formed, they are not sensitive to moisture on surfaces. Hence, the attention needed when manipulating polyisocyanates to avoid formation of carbon dioxide bubbles, leading to porosity, is not required [23]. Indeed, when PHU systems are produced, bubble formation as a result of CO₂ evolution is not observed, even in the presence of moisture. Consequently, pore-free and bubble-free coatings are easy to obtain, which is often problematic for classic PUs systems [20].

Tomita *et al.* [248] have shown that water absorption and thermal decomposition temperature of PHU films were reduced by 30 % (from 32 to 88°C), compared to conventional PU. Chemical resistance of the NIPU coatings is also 30-50 % greater than the one of conventional PU coatings. Indeed, due to their intramolecular hydrogen bonds, the carbonyl oxygen lowers the susceptibility of the whole urethane group to hydrolysis [20]. The overall permeability is also reduced to a large extent due to its nonporous nature and is 3-5 times less than conventional PU ones [249].

During PHU synthesis, different side-reaction have been reported in the literature: amine carbonation, *in situ* CO₂ synthesis production, urea synthesis, amidation reaction or oxazolidinone synthesis [250]. These side reactions could involve additional moi-

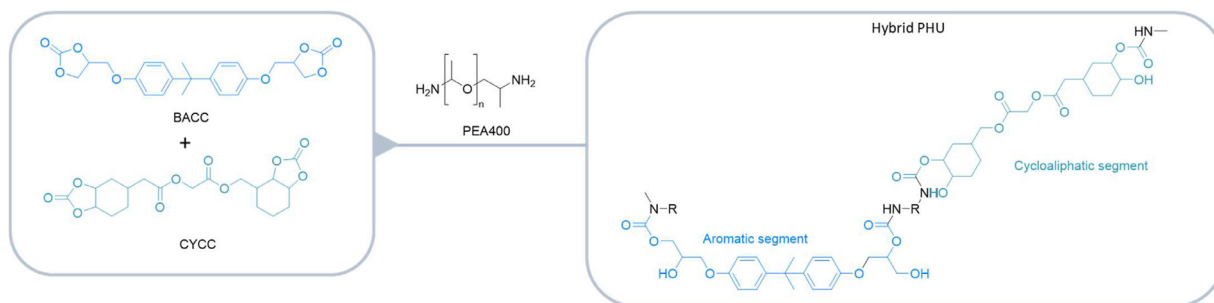
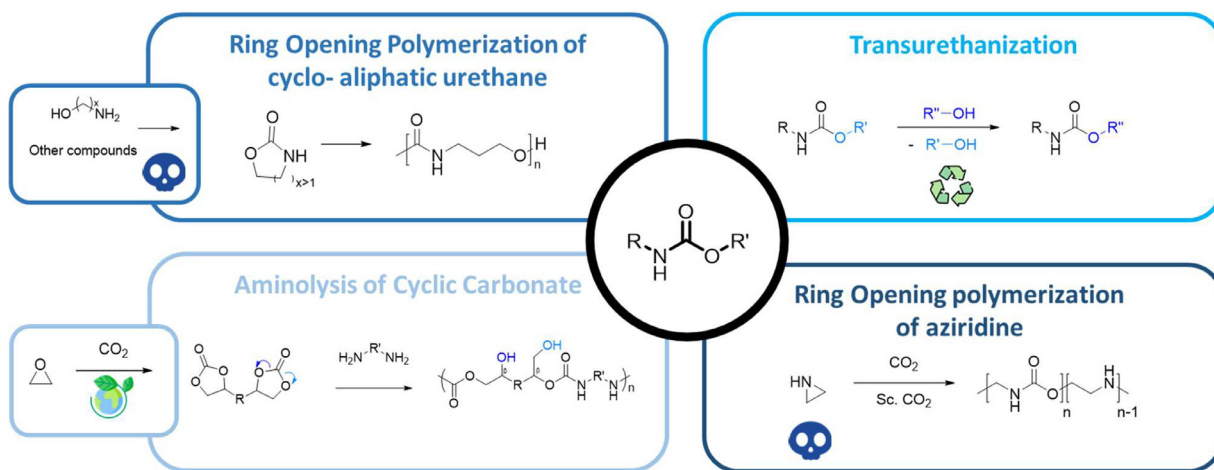


Fig. 9. Synthesis of hybrid PHU from the reaction of BACC, CYCC and PEA400.



Scheme 34. Main synthetic pathways of non-isocyanate polyurethanes.

eties from external sources, reactants, products, or internal reorganization. They must be controlled as they may cause deviation in the stoichiometry ratio and affect the desired properties. They limit the conversion by consuming reactants, often amines. Moreover, the PHU synthesis present other drawbacks: i) there is no poly-functional cyclic carbonates available on the market yet, ii) PHU synthesis is hampered by the low reactivity and the low conversions of both the amines and the 5CC, and iii) the high density of hydrogen bonds formed during the reaction leads to a high viscosity reaction media that limits PHU molar masses. This latter feature was recently shown by Benazet *et al.* [251] by studying PHU synthesis using techniques such as differential scanning calorimetry (DSC) and NMR spectroscopy. Although these issues could be solved by using catalysts or working at very high temperatures and/or with long reaction times, it would result in an increase of side reactions and thus in the loss of PHUs specific properties [252].

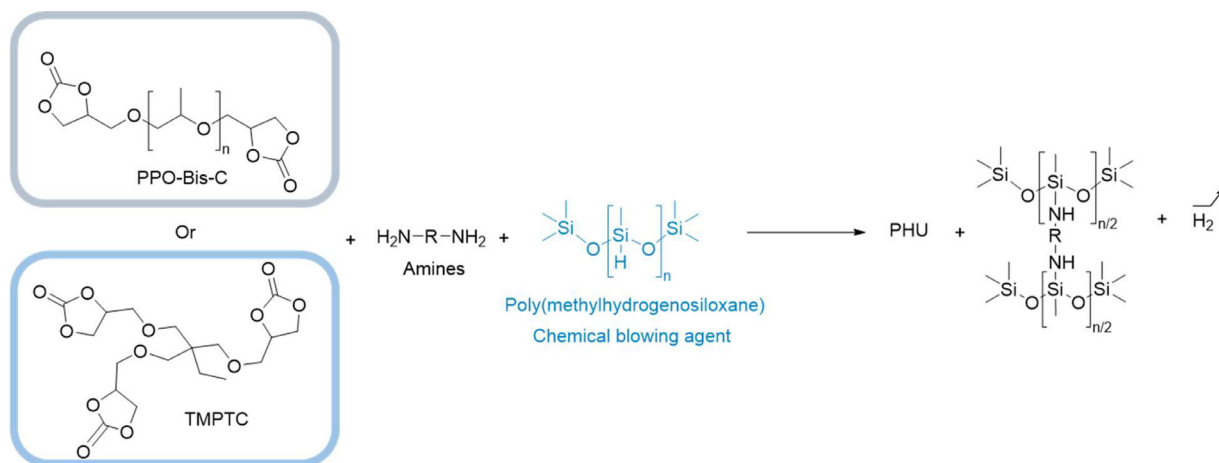
Consequently, PHUs are not close to being industrialized due to their significant drawbacks such as the lack of reactivity and the molar mass stagnation. Conventional PU have molecular masses between 40,000 and 80,000 $g \cdot mol^{-1}$ when NIPUs plateau around 22,000 $g \cdot mol^{-1}$ [224]. To solve these problems several avenues are being investigated. Most of the research is done on the cyclic carbonate. The cyclic carbonate can be either activated or enlarged. Hence, studies are done on the size of the cycle. Six, seven and eight membered cycles can be synthesized to enhance cyclic carbonates reactivity. Several groups have shown that the reactivity increases as the cycle size increases. Gomez-Lopez *et al.* [253] revealed that 8-membered CC are the most reactive. However, their stability is very low, and they are costly to produce (contrary to epoxide and carbon dioxide that are very cheap). Additionally, 8CC synthesis process requires the use of carbonylation agents like phosgene or alkyl chloroformates.

On another hand, it is possible to work on the amine moiety to increase the cyclic carbonate – amine reactivity. Quienne *et al.* [254] recently showed that β -hydroxylamine reacts much faster than aliphatic amines displaying a similar structure. They showed that the β -OH substituent is lowering the activation barrier of the reaction, as compared to the alkyl-amine, by allowing a faster proton transfer to the opened cyclic-carbonate through H-bonding support compared to the alkyl-amine.

Scheme 34 represents an overview of different NIPU synthetic routes. Even if they are phosgene-free and isocyanate-free, some of them still rely on toxic precursors such as the copolymerization of aziridines with carbon dioxide and the ROP of cycloaliphatic urethanes. Safer ways to synthesize NIPUs are nowadays the focus of attention. For instance, the transurethanization by polycondensation between a biscarbamate and a diol and the polyaddition between cyclic carbonates and amines seem to be promising approaches. According to Maisonneuve [21] and Kathalewar [23], this later method is the most attractive one. Because the formation of PHU by cyclo-carbonate aminolysis is a polyaddition, there is no by-products generated and it can be used to synthesize thermoplastics as well as thermosetting polymers. In addition, other research groups work on the synthesis of polymers with similar properties to PU but without carbamate linkages, *i.e.* by aza-Michael reaction [255].

To sum up, despite the outcomes on NIPU synthesis, many scientific and technical barriers remain to make one of these techniques pertinent for the synthesis of PU at industrial level.

Nevertheless, these reactions are the subject of an intense research at industrial level, as proven by the number of patents released each year, particularly by Chinese companies [256–261]. For instance, the Chinese institute of chemical industry of forest patented self-healing and reprocessable NIPU under mild conditions (temperature lower than 60°C for less than 2 h) by introduc-



Scheme 35. General Scheme of the formation of NIPU foams by reaction between cyclic carbonates, amines and poly(methylhydrogenosiloxane) as BA.

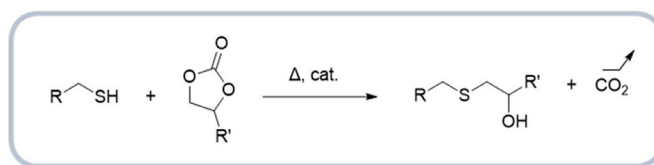
ing dynamic disulfide bridges in their material. Additionally, to the classical way of recycling them, these NIPUs can be healed from scratches on their surface with UV illumination. As an example, 91 % of the initial properties were recovered, after a sample was crushed into pieces and hot pressed at 60°C for 30 minutes under a 5 MPa pressure [262]. Henkel also shows interest in NIPU as attested by its 2020 patent reporting PHUs able to crosslink at room temperature with amidoindole derivatives as catalyst.

On the other hand, the industrialization of NIPU foams suffers off a bottleneck because of the slow kinetic of the CC - amine reaction, while the pores formation requires a fast crosslinking to trap the gas liberation. Nevertheless, research is focusing on this field, as discussed in the following section.

5.6. NIPU foams

Due to major health concerns around chemical blowing agents (BAs) (isocyanates + water) and physical BAs, researchers have focused on interesting chemical reactions that can release gas by-products to produce NIPU foams. Some of these new chemical BAs could be incorporated into the polymer network, thus avoiding the presence of residues able to migrate out of the foam. Cornille *et al.* [22] were the first ones, in 2015, to report the synthesis of NIPU foams by using poly(methylhydrogenosiloxane) as a chemical blowing agent. The NIPU foams were prepared from poly(propylene oxide)-biscarbonate (PPO-Bis-C), TMPTC and two multifunctional amines as NIPU precursors, while blowing of the foam was obtained by release of dihydrogen through the reaction between amine and SiH groups of the BA (Scheme 35). The different characterization techniques (SEM, TGA, DSC) showed that the synthesized foams are high apparent density flexible foams that exhibit T_g between -18°C and 19°C, and have a thermal stability above 300°C. Their structures and thermal properties depend on the degree of crosslinking provided by the difference of functionality of the cyclic carbonate and the amine structure [263]. Although dihydrogen is highly flammable, which prevents any use of this NIPU foam, this piece of work introduced the concept of using other types of blowing agent in combination with NIPUs.

Taking advantage of the exothermic reaction between aldehydes and amines forming imines, Chen *et al.* [264] synthesized a novel tannin-based NIPU rigid foam by first reacting mimosa tannin with DMC and hexamethylenediamine to form a NIPU resin. As prepared NIPU resin was then mixed with hexamine and set to react with of an aqueous solution of citric acid and glutaraldehyde. This led to a self-standing foam that was subsequently cured at 80°C overnight to obtain the rigid foam. Bigger pores foams were obtained with greater amount of citric acid, while increasing the amount of glu-



Scheme 36. Pearson reaction.

taraldehyde, caused a decrease of cell-wall pores. While the compressive mechanical properties were enhanced by improving the level of cross-linking between tannin NIPU molecules with higher amount of glutaraldehyde, this method presents the drawback of the high toxicity of glutaraldehyde. Another strategy to prepare self-blowing NIPU foams is through the Pearson reaction as pioneered by Monie *et al.* [265]. As seen in Scheme 36 the Pearson reaction consists in the addition of a thiol onto a cyclic carbonate, generating a thio-ether and carbon dioxide as blowing agent.

Based on the same reaction between thiol and cyclic carbonates, Monie *et al.* [266] and Coste *et al.* [267] recently reported the production of NIPU foams using blocked thiols like thiolactone or cyclic thiocarbonate to generate the thiol after reaction with an amine. Using a thiolactone, Monie *et al.* were able to synthesize rigid ($T_g = +15^\circ\text{C}$) to flexible foams ($T_g = -25^\circ\text{C}$) at 80°C for 24 h, depending on the amine used. Furthermore, these foams have the particularity to be reprocessable thanks to their OH pending groups. On their side, Coste *et al.* synthesized self-blowing foams from a mixture of a bis-cyclic dithiocarbonate compound, TMPTC and Jeffamine EDR-148 at 90°C for 24 h. These foams present two different T_g , the first one corresponding to the phase rich in thio-carbonate moiety in the range of -30°C/ -45°C and the second one corresponding to the phase rich in crosslinked carbonate in the range of 10°C/20°C. Mechanical and thermal properties obtained for these foams are in adequation with the one of Monie. Although this strategy appears effective to produce NIPU foams, the use of cyclic dithiocarbonate may be an issue since they are made from epoxy and carbon disulfide, which is CMR and highly volatile.

Moreover, the required reaction times (around 24 h) and the reaction temperature (80 – 90°C) prevent the transfer of this process to prepare NIPU foams at industrial level. Indeed, PU foams usually blow at room temperature within a few minutes, which makes their industrial production extremely competitive.

6. Green processes

Despite the intense research efforts that are put on synthesizing PU from safer and sustainable chemicals, research is also con-

ducted on developing greener processes for PU synthesis and shaping, as to comply well with the principles of green chemistry [268]. Producing PU materials using fewer toxic solvents, making materials safer to handle or from bio-based sources is a good strategy, but to lower the environmental impact of PUs, all aspects of their production must be considered. Consequently, processes must also be re-adapted, which can be done following different strategies such as eliminating the use of organic solvents (waterborne PUs, bulk polymerization or reactive extrusion) or limiting the energy input of the process (irradiation source or catalysts).

6.1. Mechanochemistry and reaction injection moulding process

Mechanochemistry is based on the application of mechanical force to, induce chemical reaction or bond activation bonds at molecular level in the solid state. Mechanochemistry is advantageous for avoiding the use of hazardous and toxic solvents, for enabling the reaction between solids that are insoluble, for decreasing the temperature and time reactions [269,270]. Mechanochemistry is a fast-growing and promising chemistry area used to design small molecules but also to drive polymerization reactions such as PU synthesis. In one of the only report of PU synthesis by mechanochemistry, Oh *et al.* [271] developed a facile solid-state mechanochemical synthesis of partially bio-based TPU through ball-milling technique. They reacted, in a stainless-steel vessel with two 15 mm stainless steel balls at 20 Hz, 2,5-bis(hydroxymethyl)furan with MDI and 3 mol % of DBTDL. After 60 min of reaction, they obtained a TPU with a maximal \bar{M}_w of 167,000 g·mol⁻¹ and a very high T_g of 96°C. They also synthesized copolymers with various amines and alcohols to modify the PU final properties. This example shows that is possible to design PU materials by mechanochemistry in a sustainable, easy, and rapid way. Since mechanochemistry is to laboratory scale what reactive extrusion (REX) is to industrial scale, mechanochemistry often provides valuable information for scale-up and production [272].

It is thus not surprising that REX is industrially employed to polymerize highly viscous polymers without the need of any solvent. It is an attractive route to polymerize a liquid or solid monomer to form a high molar mass polymer melt, tailored by various parameters: kinetic, heat transfer and reaction rate [131]. REX is thus well suited for the synthesis of PHU as reported by Magliozzi *et al.* [273] who were able to obtain complete conversion of reactive carbonate functions in relatively short reaction times (hours instead of days for classical bulk polymerization), at 230°C. Brüll *et al.* [274] also focused on REX process to obtain sustainable isocyanate-free hydrophobically modified ethoxylated PHU, with molar masses in the range of 24,000–46,000 g·mol⁻¹, within 2 h. The mixing was enhanced with REX, compared to a classical batch reactor, and the heat distribution was homogenous.

Because of their cross-linked structure, PU thermosets cannot be synthesized by REX. Nevertheless, they can be synthesized and shaped at the same time by reaction injection molding (RIM), a technique widely used at industrial level.

In RIM, the polyol and polyisocyanate are introduced separately to a metering unit where temperature and pressure are controlled. The components are then injected under high pressure into a mixing head. The formed polymer expands to fill the cavity of the mould, and cures to create a finished product [275].

The RIM enables the production of strong, flexible materials with lower temperatures and pressures. Lehmenkühler *et al.* [276] studied the process parameters to produce highly crosslinked PU. They showed that increasing the mould temperature of 20°C can increase the Young's modulus by 2 %; increasing the mass flow and the components temperatures can also improve the Young's modulus.

RIM, REX and mechanochemistry thus offer the opportunity to produce PU materials without using solvent, but most importantly, these techniques allow fast reaction and the mixing of component even with high viscosities. Given that most issues for the industrial production of NIPU arise from the slow reactivity of starting compounds or the high viscosity of the reaction media, it is surprising that these techniques have not received greater attention from the research community.

6.2. Waterborne polyurethanes

As mentioned previously, PUs display excellent chemical resistance, adhesive properties, and abrasion resistance. As such, they are very well suited for paint, coating, and adhesive applications. For these types of applications, PUs are, most of the time, solubilized in volatile organic compounds (VOC) that evaporate after application on the desired surface. Waterborne polyurethanes (WPUs) [277] have thus emerged as an eco-friendly alternative to VOC-based polyurethanes. WPUs are totally reacted urethane polymers dispersed in water, meaning that they contain no residual free isocyanate. It makes them safer and easier to use than conventional PUs. More than being environmental-friendly, WPUs exhibit similar high performances as their solvent-borne counterpart. For all these reasons, they are currently in the spotlight to be used as biomaterials [278].

According to Kim and Lee [279], WPUs are non-toxic, non-flammable, and non-polluting [280]. Moreover, they do not suffer from the increasing viscosity problem observed in solvent-based systems during the step of chain extension. Indeed, since they are dispersed in water where the polymer-solvent interactions are unfavourable, polymer chains collapse, and their molar masses increase without adversely impacting viscosity.

WPU are synthesized from the same building blocks as conventional PUs: polyisocyanate, polyol and chain extender [281]. Nevertheless, three steps are usually employed to obtain the final WPU dispersion. First, a TPU or TPU oligomer displaying isocyanate or blocked isocyanate chain-ends is synthesized in bulk or in solution (organic solvent). Second, as prepared PU, in bulk or in solution, is dispersed in water. Finally, chain extension of the PU in water is performed by reaction of isocyanates chain-ends with amines or blocked amines. In the case where an organic solvent is employed to disperse the PU in water, a last step consisting in distilling the solvent out of the dispersed phase is often applied to obtain a VOC-free WPU dispersion. Since isocyanates react with water to form CO₂ and amines, WPUs are most often poly(urethane-urea) systems. Because PUs are hydrophobic materials, hydrophilic parts such as carboxylic acids are often introduced into the polymer backbone (Fig. 10) to provide stability to the dispersed phase. Fig. 11 shows the synthesis of a WPU emulsion.

The resulting material can be called aqueous solution (colorless and transparent with particle sizes of less than 1 nm), dispersion (slightly turbid, white, and translucent, with particle sizes ranging from 1 to 100 nm) or emulsion (white and turbid, with particle sizes larger than 100 nm) depending on the appearance and the

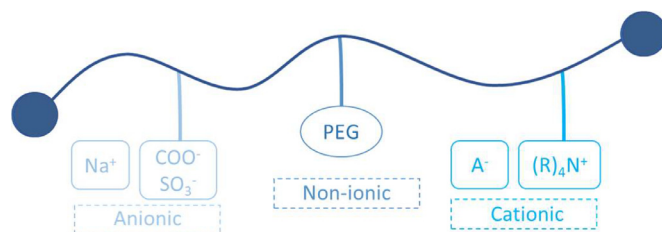


Fig. 10. Different types of hydrophilic groups attached to the prepolymer chain.

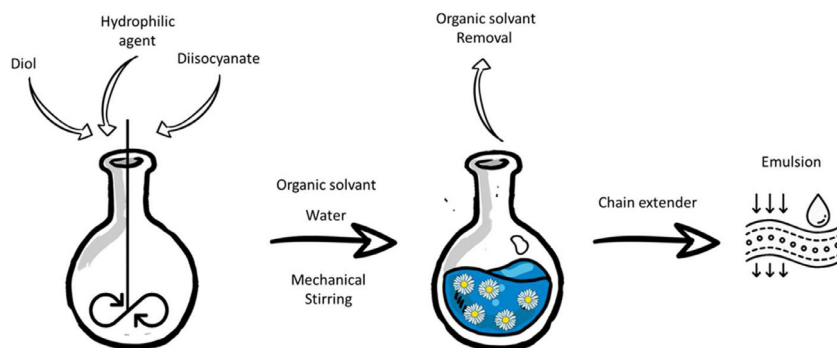


Fig. 11. Synthesis of WPU emulsion.

particle size [282]. It exists four dispersion processes: the acetone process, the melt dispersion mechanism, the prepolymer mixing process and the ketimine, ketazine processes [283].

The acetone process is the most popular strategy and consists in the addition of an internal emulsifier containing an acidic group. This process uses an organic solvent miscible to water with a relatively low boiling point, such as acetone or methyl ether ketone (MEK) [284]. By progressively adding water to the prepolymer solution, an emulsion is created. At last, all the solvent will be removed by distillation.

The prepolymer mixing process is based on the hydrophilic modification of prepolymer terminated by isocyanate moieties. This prepolymer is mixed with water to form an emulsion. This process avoids the use of large amount of solvent but is only suitable for low viscosity prepolymers [283]. A chain extender (di- or polyamines) is then added to the aqueous dispersion at relatively low temperature to avoid side reactions between isocyanate and water.

In the melt dispersion process, the prepolymer reacts with an excess of ammonia or urea, leading to a prepolymer with terminal urea or biuret groups. Chain extension is achieved by methylation of the biuret groups with formaldehyde. This reaction does not need any organic solvent but is conducted at temperature higher than 100°C to reduce the viscosity of the melted prepolymer.

The ketimine and ketazine processes consist in reacting a blocked diamine and a blocked hydrazine with ketones resulting in ketimines and ketazines, respectively. The main advantage of this process is the characteristic of these molecules that are inert toward isocyanates. These are mixed with the prepolymer containing ionic groups, avoiding premature extension.

Many variations of these basic processes have been reported. For example, in the acetone process, chain-extension can be performed before dispersing the PU in water. In addition, various compositions have been employed to prepare WPU dispersions. In particular, the use of bio-based polyols or isocyanates to synthesize bio-based WPU dispersions has been the subject of intense research activity over the last few years [277]. Taking into consideration the benefits of this technology both on environmental and safety aspects, it is for sure that it will be the subject of an intense research over the next few years.

6.3. UV cross-linking

The attention towards UV-curable coatings is continually increasing due to their fast curing and low energy consumption when using Light Emission Diodes as irradiation source [285]. Their formulations are usually composed of three major components: a photo-initiator, a reactive oligomer, and a reactive diluent (used to reduce the viscosity of the formulations and to tune the cross-linking density of the final material) [286]. However, these

resins are prepared using a conventional process, which employs polyisocyanates and polyols as raw materials.

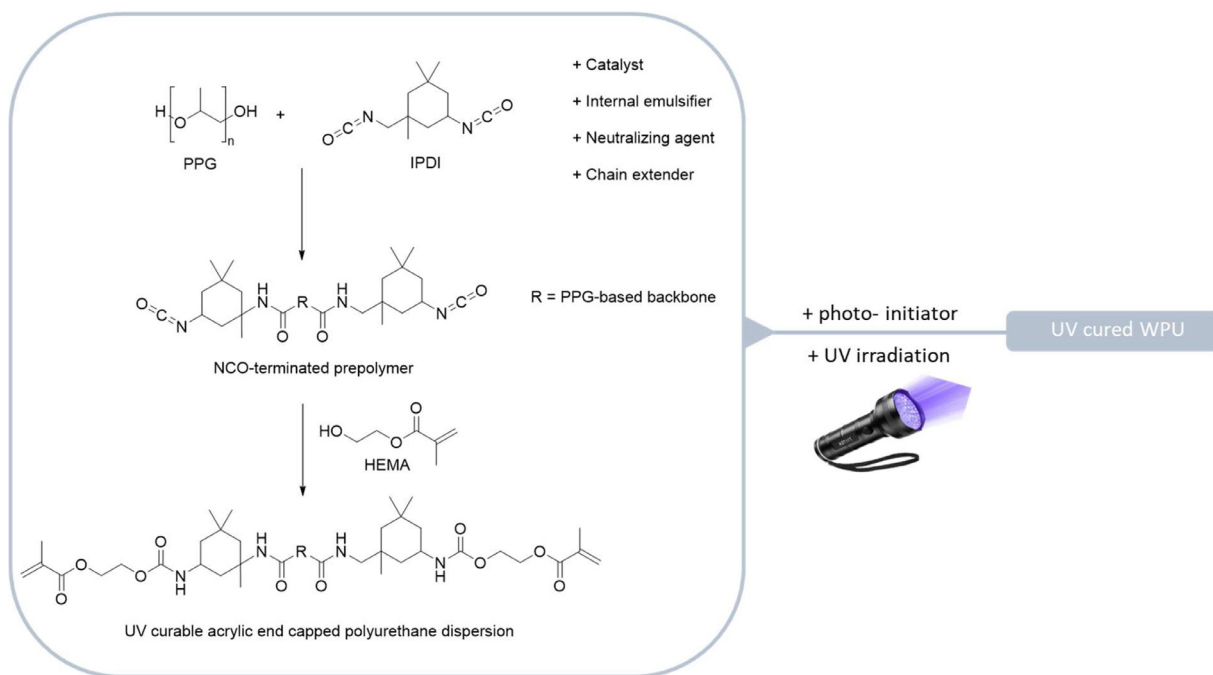
Llorente *et al.* [287] were the first to introduce UV curable acrylic end-capped polyurethane dispersions to improve conventional WPU performances and overcome the drawbacks of traditional UV curing such as solvent volatility, smell, and toxicity. To this end, they first synthesized WPU based on IPDI, PPG and additives such as catalyst, neutralizing agent, and emulsifier. In the second step, they prepared an acrylic end-capped prepolymer by adding 2-hydroxyethyl methacrylate (HEMA) in the water/acetone solution. Finally, acetone was removed to obtain a UV curable acrylic end capped polyurethane solid dispersion. Almost all the elements were gathered to perform UV curing except the photo-initiator, 1-hydroxycyclohexyl phenyl ketone, which exhibits three UV absorption bands at 240, 280 and 340 nm (Scheme 37). Finally, they dissolved the photo-initiator in acetone and added it to the dispersion. After evaporating the water from the samples at room temperature overnight and then 2 h at 80°C, they were able to obtain a UV cured PU materials using a 254 nm UV lamp, and could characterize it. Unfortunately, they did not compare the performances of the resulting material with non-UV curable WPU counterparts.

Boisauvert *et al.* [226] also investigated the possibility to design NIPU UV-curable system. In their work, an acrylate-terminated PU oligomer was prepared by transurethanization reaction of an excess of poly(tetramethylene oxide) (PTMO) with hexamethylene dicarbamate (BMC-C₆) followed by reaction with acryloyl chloride, as depicted in Scheme 38.

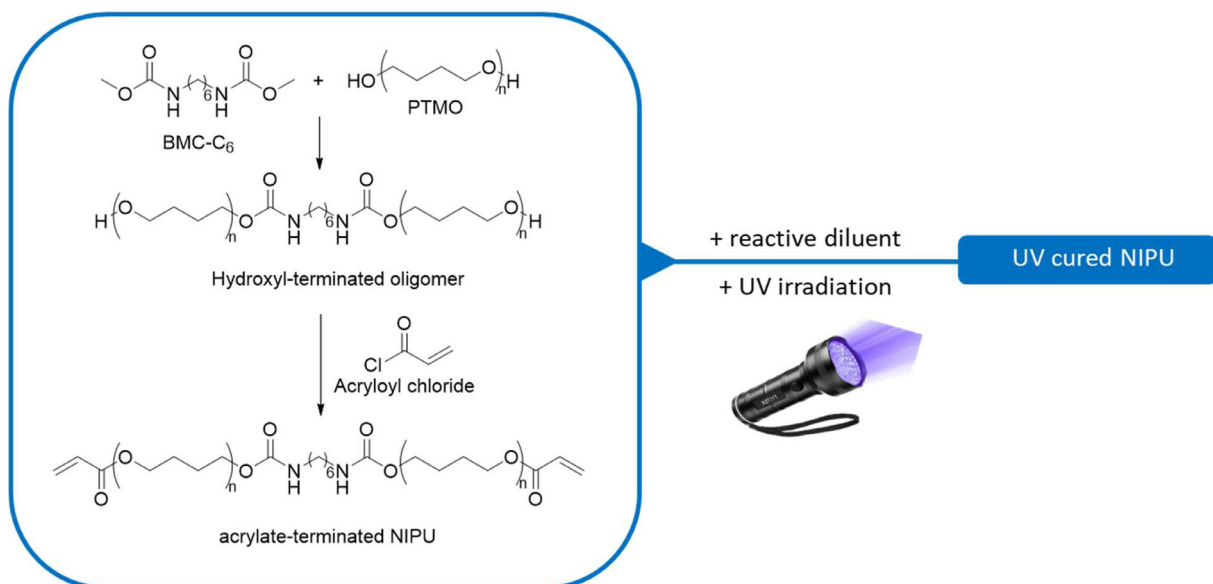
To prepare the UV-curable formulations, various reactive diluents were used: hexamethylenediol di-acrylate, urethanediol dimethacrylate and N-hexamethylene dihydroxyethyl carbamate diacrylate. The obtained properties were in consistency with those of the flexible PUs currently developed in the market: Young Modulus $E_Y = 2.69\text{--}25.5$ MPa, breaking stress $\sigma_r = 3.62\text{--}11.8$ MPa, and elongation at break $\varepsilon_r = 56\text{--}470$ % [226]. They showed that the system could be tunable through the length and chemical structure of the acrylate oligomer and reactive diluent, as well as the crosslinking density, offering a wide range of possible properties.

Additionally to these oil-based PU UV-curable systems, many bio-based formulations have been developed following the same strategy [288]. Vegetable oils were found particularly useful because its structure can be easily modified or already possess diverse functionalities such as hydroxyl, unsaturation, carboxyl, and epoxy, as mentioned before. As such, they offer the opportunity to vary (meth)acrylate contents and thus cross-linking density.

Besides using acrylate-terminated PU oligomers to produce cross-linked PU coatings under UV irradiation, it is also possible to trigger the direct cross-linking of isocyanate/alcohol mixtures at room temperature under UV irradiation by using photo-base gener-



Scheme 37. Synthesis of UV curable acrylic end capped polyurethane dispersion.



Scheme 38. UV cross-linking approach of acrylate-terminated NIPU.

ators to release an amidine catalyst, as demonstrated by Zivic *et al.* [289].

UV-curable PU coatings can thus be synthesized from various starting compounds, either from (meth)acrylate-ended PU formulations comprising a radical photo-initiator or directly from isocyanates and polyols when combined with a photo-base generator. Interestingly, in addition to provide weathering and chemical resistant coatings, most of these formulations can also be cured in stereolithography systems to produce objects as described in the following part.

6.4. Printing

In addition to basic applications and due to their excellent mechanical strength and time durability, PUs are also used for ad-

vanced technologies such as 3D printing. This process is promising for environmental sustainability as it relies on the layer-by-layer deposition of materials, without overconsuming feedstocks, which limits the material wastes during production. Additive production is beneficial regarding waste generation in contrary of the subtractive production which consists in transforming a solid material block by progressive removal of material [290].

The 3D printing offers many advantages in various fields, and specifically in biomedical applications since it allows fast fabrication, high precision, and customized production. There are a variety of 3D printing methods and the most used for the production of objects made of PU are photo-polymerization based ones like stereolithography (SLA) [291] or digital light processing (DLP) [292], powder bed fusion such as selective laser sintering (SLS) [293].

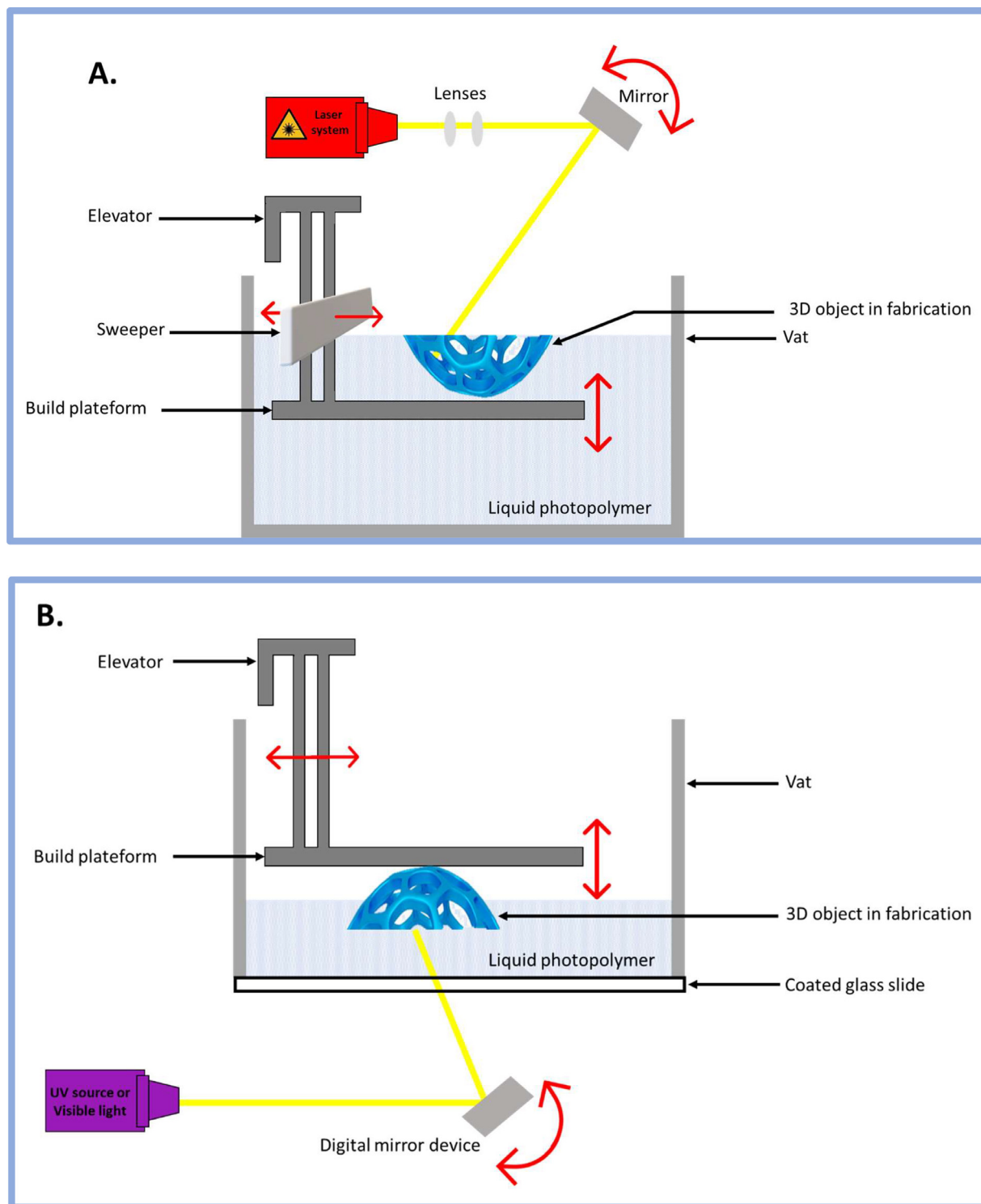


Fig. 12. Schematic representation of SLA (A) and DLP (B) techniques.

Nevertheless, other methods based on extrusion for instance fused deposition modeling (FDM) [294] but also power bed and inkjet head 3D printing [295] or liquid-frozen deposition manufacturing (LFDM) [296] have also been employed for PU printing.

Polymerization by SLA (Fig. 12-A) is the first fast prototyping process which was developed in the 80's. The SLA of PUs relies on PU prepolymers terminated by acrylates moieties that are subsequently photo-crosslinked under UV-irradiation in the presence of radical photo-initiators. The acrylate-terminated prepolymers are

called poly(urethane-acrylates), commonly noted PUAs. PUAs are usually synthesized by reacting PUs prepolymers terminated by isocyanate moieties with HEMA. In addition to the intrinsic toxicity of acrylates, such PUAs contain residual traces of isocyanates. In the current context of human and environment wellbeing, synthesis routes of innocuous and bio-based PUA have been investigated as described in the previous section.

DLP (Fig. 12-B) is very similar to SLA, the major difference is that SLA technology uses a laser that build layer-by-layer the 3D

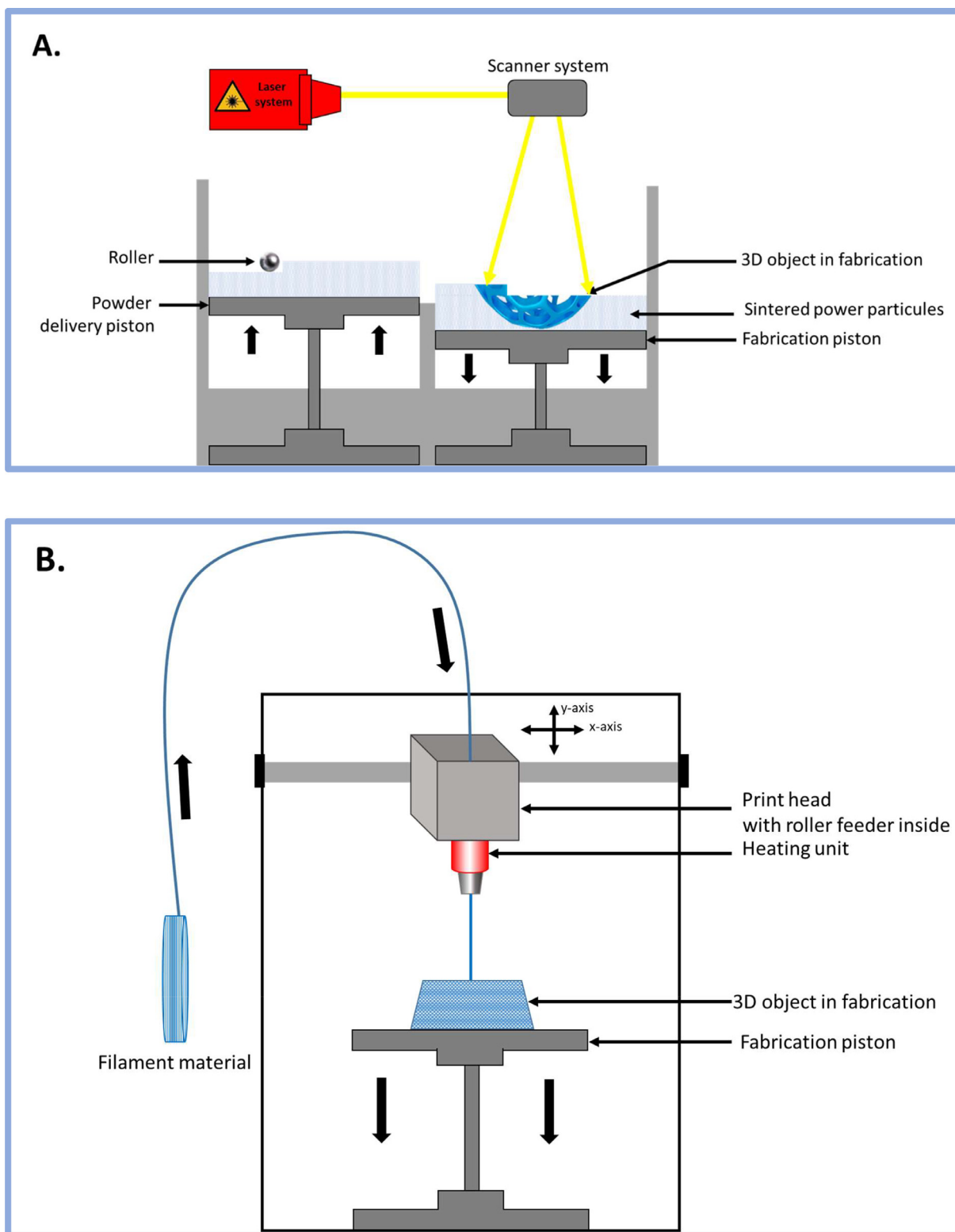
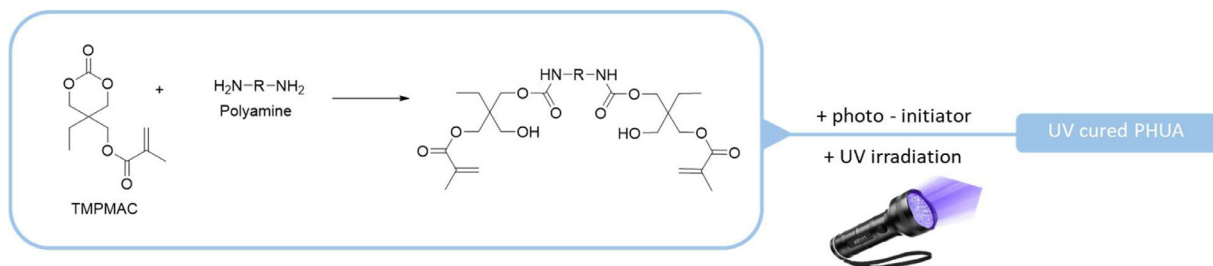


Fig. 13. Schematic representation of SLS (A) and FDM (B) techniques.

object, a DLP machine uses a projected light source (UV or visible light) to cure a single image of the layer across the photo-polymer liquid at once. As SLA, DLP is a technic used in biomedical field. For example, Chen *et al.* [297] synthesized PCL-based polyurethane acrylate prepolymers to print, tissue scaffolds with very precise pore size. SLA and DLP techniques allow to obtain complex 3D objects with a high-resolution structure. However, one drawback of

these methods is that they are just few biomaterials for bioink that can be photo-cured.

SLS (Fig. 13-A) is one of the mainstream 3D printing techniques. Like with photo-polymerization, it consists in making a material layer-by-layer by fusing powders particles together with a high energy laser, which means that no liquid is used. The main disadvantage of this technic is that the obtained objects are porous and



Scheme 39. UV cross-linking approach of PHUAs for 3D printing application.

generally need to be coated or hot isostatic pressed (which means that high temperature and pressure of inert gas is applied) before end.

Extrusion by FDM (Fig. 13-B), consists in laying melted thermoplastic filaments next to each other, then on top of each other, making them merge thanks to the high temperature ($160^{\circ}\text{C} < T < 400^{\circ}\text{C}$) of the melted polymer. The cooling down of the material enable the production of a 3D structure.

Since 3D printing can be used to create complex structures, some researchers worked on designing PU-based foams. Gama *et al.* [298] have prepared 3D printed composite foams for thermal insulation applications. They used cork to enhance the properties of the 3D printed composite foams and FDM technique. To this end, commercially available TPU was mixed with cork powder and the mixture was then extruded to obtain a 3D printable filament. They proved that, due to the presence of cork, the resulting foams exhibits lower density ($316 \text{ kg}\cdot\text{m}^{-3}$ with no cork and $245 \text{ kg}\cdot\text{m}^{-3}$ with 5 %wt of cork), lower thermal conductivity ($0.49 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ with no cork and $0.49 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ with 5%wt of cork) and are more flexible (elongation at break of 61 % with no cork and 53 % with 5 %wt of cork). Based on the extrusion process, Fomicon, a Belgian based company specialized in portable PU systems, has developed a 3D printing system bases on the spraying of PU foam. In an automated environment, where a robotic arm is installed and connected to a computer, PU foam can be printed over surface for insulation purposes. This method allows to know after few seconds the deposited volume and consequently, if it is necessary or not to add a new layer depending on customer's specific needs. However, this technic compared to conventional spraying of PU foam presents multiple drawbacks since the installation of the system and, the time of execution are quite long and the resulting price quite high. Since 3D printing is a technic that takes time and can be very expensive, it should be set to the conception of high-valued products such as biomaterials.

Among the last achievements using photopolymerization to build objects, Pyo and Wang [299] synthesized the first green poly(hydroxyurethane-acrylate) (PHUA) using methacrylate-functionalized six-membered cyclic carbonate and biogenic amines such as putrescine or cadaverine to perform DLP-based 3D printing (Scheme 39). Indeed, the resulting functionalized diurethane monomers were 3D-printed via UV-activated free radical polymerization of the methacrylate group to form crosslinked PHUAs in biologically relevant structures.

Despite this breakthrough, this strategy is still relying on molecules with a recognized toxicity: methacrylates. To avoid these drawbacks, new strategies must be developed to obtain PHUs using light stimuli. Zivic *et al.* [289] developed three new photo-base generators based on a thioxanthone chromophore to synthesize PU from commercially available polyols and polyisocyanates. They prepared at room temperature 3D printed PU figures using light as an external trigger. Another limitation of this technic is that some monomer can be trapped in non-printed volume (eggshell like structure). Most of the time, a post curing is needed, but the

main advantage of this technic is the fact that it allows to print complex structures and that the non-polymerized formulation is reusable.

WPU can also found application in 3D printing. Hung *et al.* [300] have synthesized a novel biodegradable waterborne PU in the form of nanoparticles by a water-based process. 3D printing was made from LFD system by building the scaffold layer-by-layer. Not any toxic organic solvent, crosslinker or initiator was used. The scaffold was printed from a feed containing PU-nanoparticle dispersion and polyethylene oxide (PEO). The process generated a nontoxic, biodegradable and highly elastic scaffold with superior cytocompatibility.

In addition, Huang *et al.* [301] synthesized a new biodegradable waterborne PU with polycaprolactone and PLA chains that was used as a bio-ink for 3D printing cell-laden tissue constructs for neural tissue engineering. A viscosity enhancer, PEO, was added to the mixture in different ratio to fabricate scaffolds. They studied the surface morphology, mechanical properties and degradation rate of the materials and showed their potential use as cartilage scaffolds.

Naturally all acrylates resins mentioned before can also be employed in other photopolymerization based technologies such as the CLIP the continuous liquid interface production technology (CLIP), originally developed by DeSimone *et al.* and now owned by Carbon3D. This technology mainly relies on an oxygene-permeable membrane placed at the bottom of the resin tank that allows inhibiting the polymerization at bottom of the tank transparent to UV, thus avoiding the need to pull the support out of the resin tank as in other technologies [302]. Compared to SLA and SLS that grow the object layer by layer, the CLIP method grows objects from a pool of resin at speeds 25-100 times faster, allowing the production of parts in minutes instead of hours.

Considering all the above examples, 3D printing is a good option to make PU greener, by removing the solvent (bulk system), using water (3D printing WPU) and reducing waste. It was also demonstrated that it is possible to use PHU to perform 3D printing showing that chemical improvements can be linked to greener processes.

6.5. Catalysts

Besides the different processes that have been described in the previous sections, catalysts play also an important role in making PU environmentally-friendly by shortening reactions times and/or lowering reaction temperature, thus saving energy. Among conventional catalysts, DBTDL, stannous octoate, 1,4-diazabicyclo[2.2.2]octane (DABCO), N,N'-dimethylpropylene urea and 1,8-diazabicyclo[5.4.0]undec-7-ene are the most used. However, many of these catalysts are toxic and have been withdrawn under legislation placed on industry, such as RoHS and REACH regulations. Residual catalysts in PU structure can lead to side reactions which could also produce toxic compounds. It is a huge drawback when the material is used in biomedical applications.

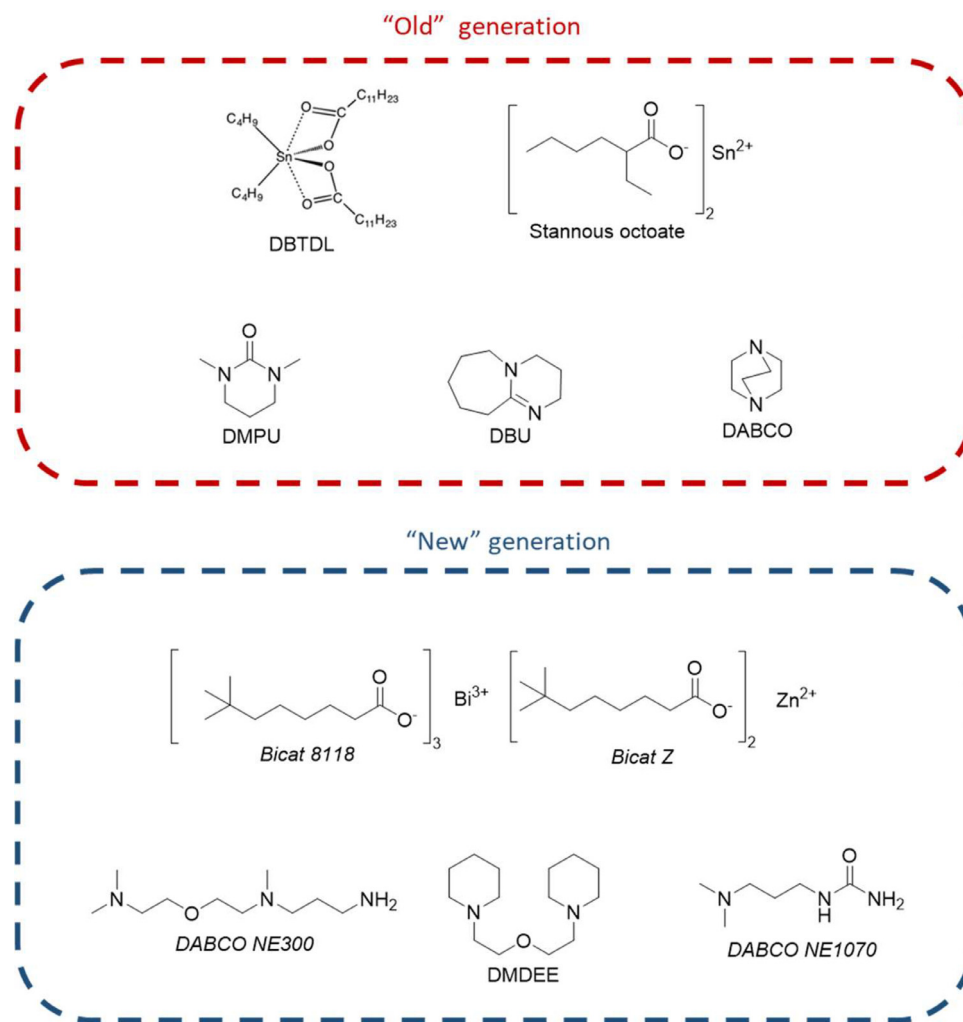


Fig. 14. Catalysts structures classified as “old” or “new” generation. Tradenames are in italics.

Nevertheless, catalysts classified as hazardous to health and environment can be authorized in small concentration in formulations. For example, morpholine diethyl ether is a good blowing catalyst used in PU foam systems. Up to 10 % of this organocatalyst can be used in PUF formulations without having to expose any hazardous pictograms on the formulation safety data sheet. Balance can thus be found between concentration and toxicity risks.

A new generation of safer and greener catalysts tend to replace toxic conventional catalysts *i.e.* tin-based catalysts. Bismuth and zinc carboxylate catalysts are promising compounds that can accelerate the reaction between polyisocyanates and polyols without promoting any detrimental side-reactions. Bismuth decanoate and zinc decanoate are respectively commercialized under the trade name Bicat 8118 and Bicat Z. They are not classified as physical and health hazards products. Moreover, at academic level, Lazzeri *et al.* [101] employed a new generation of catalysts. These catalysts reduce emissions as the molecules can chemically bind themselves to the PU matrix. Among these greener catalyst alternatives, the following can be mentioned: 3-dimethylaminopropyl urea (tradename: DABCO NE1070, gelling agent) and N-[2-[2(dimethylamino)ethoxy]ethyl]-N-methyl-1,3-propanediamine (tradename: DABCO NE300, blowing agent). Furthermore, these two molecules contain non-reactive amines that can be released from the foams once they are produced.

In Fig. 14, the structures of the mentioned catalysts are detailed. They are also classified as “old” or “new” generation catalysts.

Safer and greener catalysts for urethane formation can be used to replace highly toxic conventional catalysts. Tin-based catalysts can mainly be replaced by bismuth and zinc-based catalysts. However, legislative regulations are still evolving and thus, limit more and more the accepted catalysts concentrations. Moreover, the regulations that classify those catalysts as non-hazardous nowadays could change in the following years and become more restrictive by classing them hazardous. The development of catalysts that are safe, efficient and specific to one reaction (alcohol/isocyanate for instance) is thus necessary.

7. End-of-life management

PU are designed for long-term applications due to their highly resistant urethane linkages [50]. Nonetheless, these identical characteristics that assure durability can produce enduring environmental pollution when PU materials are mishandled and disposed of in natural surroundings. The disposal of consumer products has led to globalized pollution, particularly in Europe and North America. These countries account for 50 % of the worldwide consumption of polyurethane (PU), resulting in approximately 3 million tons of PU waste generated annually in Europe [303]. Consequently, many researchers expressed an urgent need to gather data about the persistence and pollution of plastics goods [304,305]. Historically, three main disposal methods were applied to deal with PU

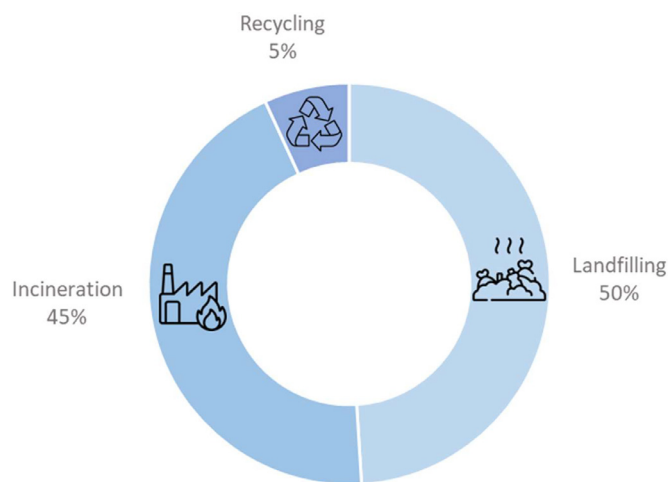


Fig. 15. Current worldwide PU waste management.

wastes: landfilling (50 %), incineration (45 %) and recycling (5 %), as shown in Fig. 15.

Nevertheless, these trends are about to change due to the global implementation of legislative regulations concerning the management of land-based waste. For instance, in Europe, the proportion of municipal wastes sent to landfills will be limited to 10 % by 2035 [306]. As a result, new methods for managing PU wastes must be investigated to prevent the burial of tons of PU-based materials. Given the present state of PU waste management, decreasing dependence on landfills would result in a significant increase in the incineration or recycling of these materials. For exam-

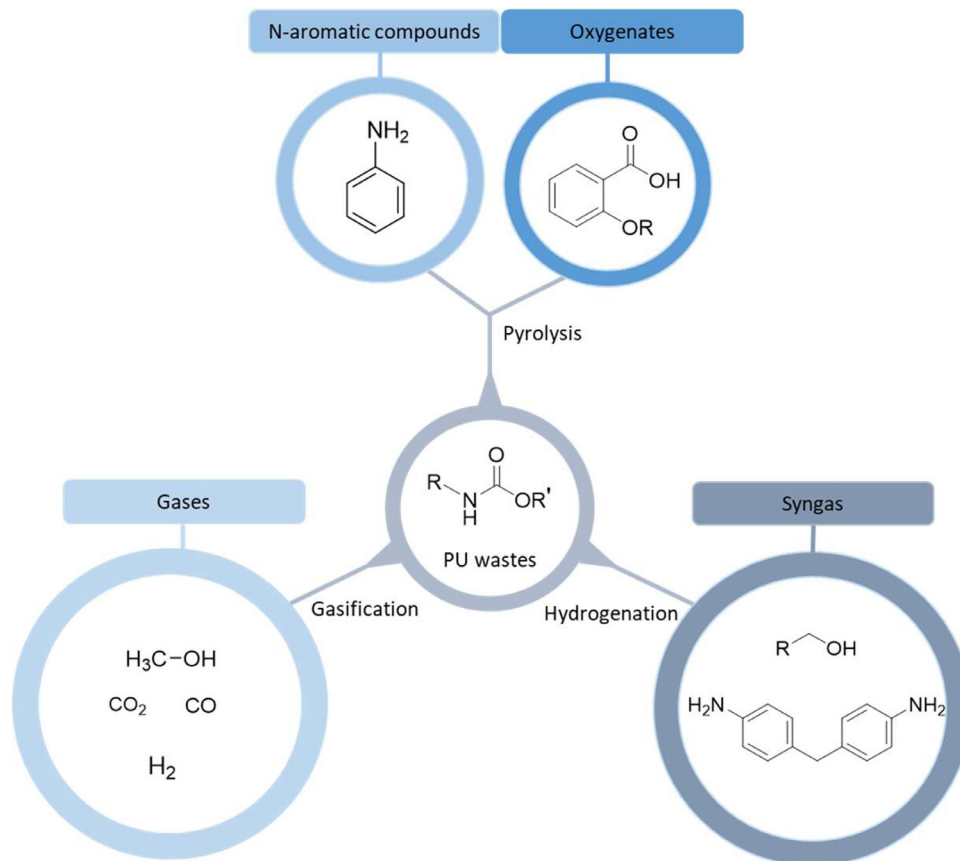
ple, European countries that set up more severe landfill restrictions have, on average, higher recycling rates of plastic post-consumer wastes [305,307]. Various PU recycling methods are documented in the literature, including energetic valorization, chemical, and enzymatic recycling. The following section discusses the energy and environmental costs based on life cycle analysis (LCA) data for each method, the volume of recycled products, and the feasibility of implementing these recycling approaches on a larger scale.

7.1. Thermochemical degradation

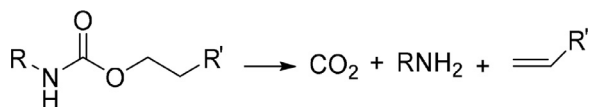
Energy recovery is a well-established technology for converting plastic waste into low molar mass molecules that can be subsequently reused in plastic synthesis and for heat generation. Vollmer *et al.* [308] demonstrated that PU can be pyrolyzed into CO and CO₂. Currently, three primary methods are employed for thermal degradation: pyrolysis, gasification, and hydrogenation. These methods are differentiated by three key parameters: temperature, pressure, and the type of gas used in the combustion process. The thermochemical recycling methods are presented in Scheme 40 and will be detailed in the following subsections.

7.1.1. Pyrolysis

Pyrolysis is a process involving the thermochemical decomposition of PU waste, wherein long polymeric chains are transformed into lower molar mass molecules under anaerobic conditions at elevated temperatures. In the literature, two stages of degradation are commonly reported. The first stage corresponds to the decomposition of polyol, while the second involves the disintegration of urethane. Rotival *et al.* [309] demonstrated that approximately 70 % of mass loss of the PU occurs between 250°C and 450°C with a secondary loss occurring between 450°C and 650°C. Zevenhoven



Scheme 40. Three main PU recycling thermochemical methods.



Scheme 41. Mechanism of PU pyrolysis.

et al. [310] pointed out that the thermal dissociation temperature ranges are dependent on the specific linkages within PU waste. For instance, urethane decomposition occurs at higher temperatures than urea, and urea decomposes at higher temperatures than biuret. The gases and molecules generated during the decomposition of PU materials are typically monitored using thermogravimetric analysis (TGA), coupled with Fourier-transform infrared spectroscopy (FTIR) and matrix-assisted laser desorption ionization-time of flight (MALDI-TOF). These analyses help in identifying the various decomposition products and elucidating the mechanisms underlying polyurethane degradation during pyrolysis. According to Ketata *et al.* [311], PU releases aromatic amines, ammonia, benzonitriles, and hydrocyanic acid under an inert atmosphere. In contrast, the polyol portion is fragmented into small oligomers containing 5 or 6 carbons. One of the mechanisms described by Ketata *et al.* is shown in Scheme 41.

Due to the variability of the resulting products, as highlighted by Font *et al.* [312], the valorization of these molecules appears to be complex. Eschenbacher *et al.* [313] developed a model for the formation of oxygenates and nitrogen compounds as a function of temperature. They demonstrated that it was possible to primarily recycle carbon residues at 300°C and then recycle 4,4'-methylenedianiline (MDA) at 500°C. They are presently conducting experiments using a catalyst to enhance the recovery of benzene and toluene from the pyrolysis process. Since these compounds are commonly used in PU synthesis, discovering ways to recycle them could contribute to a more comprehensive circular economy. Nevertheless, some of the molecules produced pose significant toxicity concerns, as highlighted by Deng *et al.* [314]. The substantial presence of ammonia (6 %^{wT}) and hydrogen cyanide (2.9 %^{wT}) at the end of pyrolysis at 850°C cannot be disregarded and presents a notable problem.

7.1.2. Gasification

The process of gasifying PUs is a highly exothermic reaction that leads to the oxidation of chemical compounds, resulting in the formation of a gas known as syngas, primarily composed of carbon monoxide, hydrogen, and ash. Gasification occurs in an oxygen-rich environment at temperatures ranging from 1,200 and 1,500°C, under pressure of 20 to 80 bars, with a residence time of just a few seconds, achieving a conversion rate of 98–99 % to gas. Syngas can serve as an energy source and also as a raw material for various chemical processes in the industry, enabling the production of methanol, ammonia, acetic acid, and carbohydrates [315]. The addition of a catalyst and control over the input air stream in the autoclave can enhance the volume of gas produced during gasification. Indeed, Guo [316] and Mark [317] found that the optimal gasification yield for waste rigid PU foams is reached using sodium hydroxide as the catalyst representing 12.5 % weight of the raw material. The operating air flow rate is 120 L·h⁻¹ at 1,000°C [316]. Mark *et al.* [317] emphasized that despite the potential for methanol and other chemical feedstock production, the industrial utilization of PU waste through gasification remains extremely limited at present. Out of the 365,000 tons of PU waste captured annually by the sector, only 2,000 tons are recovered through gasification. The majority of the waste (200,000 tons of PU waste each year) is actually used for energy recovery alongside municipal waste. This is primarily due to the insufficient quantities

of PU waste streams, making them unsuitable for recycling through gasification processes.

7.1.3. Hydrogenation

Hydrogenation is a process similar to pyrolysis, but instead of using an inert gas, it operates at 450°C under high-pressure hydrogen flow, typically within the range of 150 to 300 bars. This process results in a mixture of oil and gas known as syncrude [317]. Catalysts can be employed to enhance the reaction rate and control the product's structure, as demonstrated by Gausas *et al.* [318]. They aimed to depolymerize PU waste (both rigid and flexible PU foams) into aniline and polyol fractions using a commercially available catalyst: the ^{iPr}MACHO complex. Among the Ir-, Mn-, and Ru-commercial Ir-^{iPr}MACHO complexes, all of which exhibited quantitative and comparable conversions for PU waste hydrogenation, they found that the Ir-^{iPr}MACHO complex leads to the highest amount of aniline. Hydrogenation was conducted under 30 bar of hydrogen, at temperatures between 150°C and 180°C, resulting in polyols and isolated anilines that can serve as precursors for the synthesis of new PU materials. Zhou *et al.* [319] mentioned that it is possible to perform hydrogenation on other feedstocks than PU such as polyamide 6,6.

These thermochemical recycling techniques hold the potential for interesting environmental and economic prospects. Some various chemical feedstocks can be recovered from the processes: methanol, dihydrogen, carbon dioxide. Nevertheless, the streams of PU waste are generally mixed with household wastes due to a lack of sorting plastics from other residues. Thus, PUs cannot be properly thermochemically valorized with the technologies described above. Furthermore, the release of toxic gases makes their implementation in the industry difficult. Finally, even if these technologies allow to bring energy through the process, energy recovery techniques generate high greenhouse gases emissions, resulting in a poor competitiveness compared to other plastic waste valorization methods as highlighted by Schwarz *et al.* [320]. A more significant reduction of CO₂ emissions can be achieved by employing mechanical recycling techniques as underlined by Khoo *et al.* [214] and the McKinsey report [321].

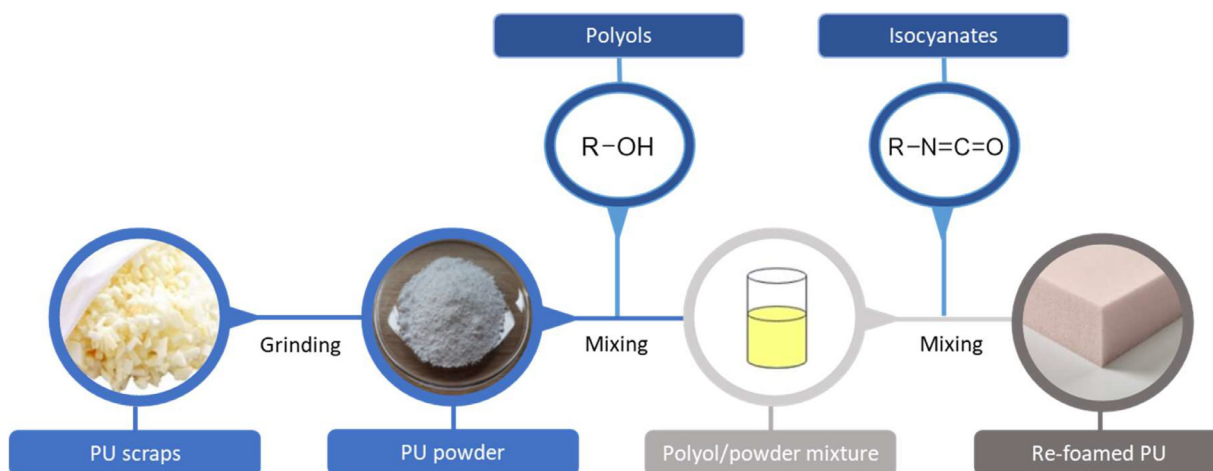
7.2. Mechanical recycling

Among all plastics recycling techniques, one of the most efficient is mechanical recycling [214]. It essentially involves reusing PU in its polymer form without undergoing chemical breakdown. The PU is reduced into powder or chips, and the fractured bonds on the surface can subsequently serve as polymerizing sites. The resulting particles are reused in production, usually mixed with other binders to create new PU materials. Among all mechanical recycling techniques, regrinding is the oldest method in PU waste recycling history [322].

7.2.1. Regrinding

Regrinding is a process that can be described as the reuse of ground PU wastes as fillers into other PU products such as elastomers or foams. It mainly involves two steps: (i) grinding PU waste into a powder, and (ii) blending the PU waste powder with a polyol to synthesize new PUs. It is estimated that a maximum of 15–25 % of polyols can be incorporated into the powder to create recycled PU [310]. The process is illustrated in Scheme 42.

The percentage of polyol mostly depends on the initial isocyanate used to synthesize the PU material: 15 % of polyol is incorporated to MDI-based powder while 25 % of polyol is added for TDI-based powder. Moreover, the granulometry of the powder impacts the whole process. The finer the powder, the lower the viscosity of the polyol/PU powder mixture, allowing for a larger



Scheme 42. General scheme of the regrinding process to recycle PUs.

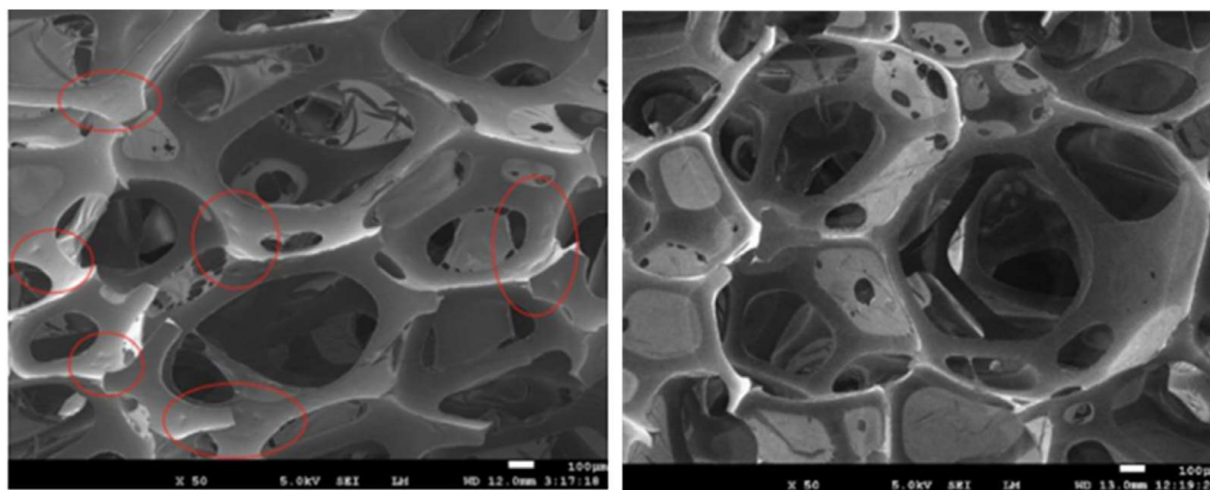


Fig. 16. SEM photographs of recycled PUR foams by regrinding process, recycled PUR foam on the left and the original PUR foam on the right, magnification $\times 50$. [325], Copyright 2023. Reproduced with permission from Multidisciplinary Digital Publishing Institute.

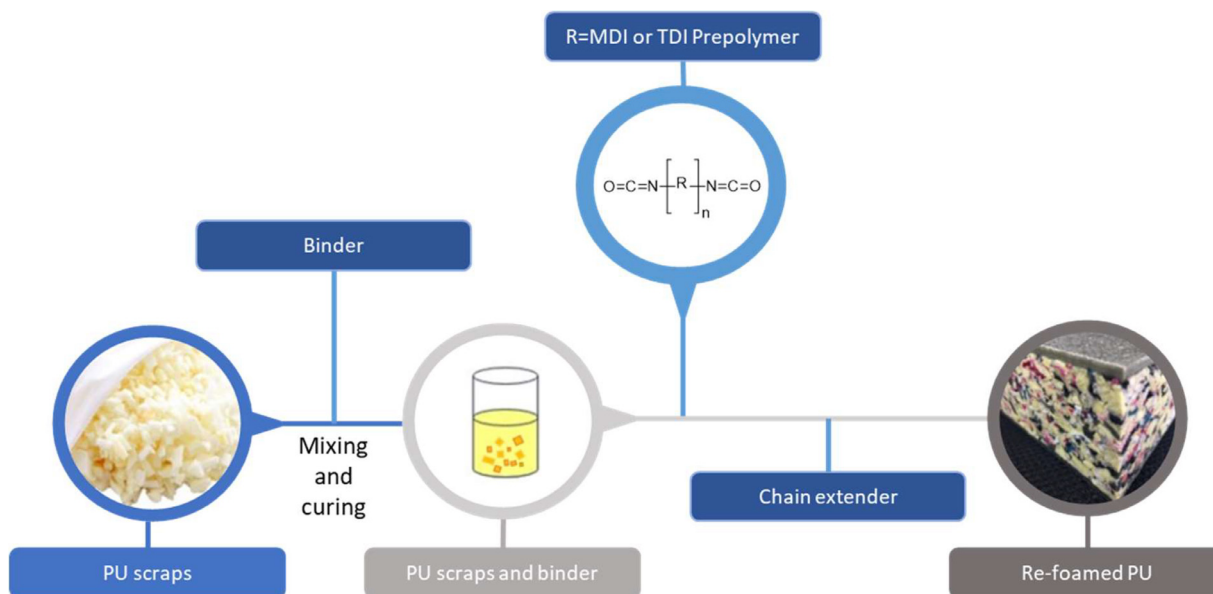
quantity of PU waste to be recycled [323]. However, the physical properties of recycled PU materials are generally lower than the initial ones. Indeed, the material may experience a reduction of up to 10 % in its mechanical properties, specifically in terms of tensile strength, according to Stone *et al.* [323]. Nonetheless, it is often feasible to maintain the density of foams, enabling their use in the same applications, especially in high-tech applications. Indeed, A. Rodrigo-Bravo *et al.* [324] highlighted that recycled PU based gypsum ceiling tile was a more sustainable material compared to the standard one. They relied on LCA categories namely global warming potential (GWP), eutrophication potential, abiotic resource depletion and the use of energy and fresh water to give their conclusions. The PU rigid foams waste came from the manufacture of insulation panels. They could incorporate 4.9 % of recycled PU foams in tiles, without altering the physical properties (thermal conductivity and noise reduction coefficient). Regarding the end-of-life of gypsum tiles, their study highlighted that when recycled PU-gypsum tiles are disposed of in a landfill alongside traditional panels, they produce 31 % less non-hazardous waste. Recently, Guo *et al.* [325] studied the mechanism of PU regrinding process. They showed that a mechanochemical cleavage was occurring during the operation, leading to the formation of new hydroxyl and amino groups at the surface of the recycled material. Nevertheless, small deformations on re-foamed PUs are noticeable on SEM photographs, highlighted in Fig. 16 in red circles.

This is mainly due to the hydroxyl groups in the powder that remain unactive as new reactive groups are created only on the surface of the material. These little defaults lead to lower mechanical properties. Nevertheless, the re-foamed PU recycling show really good properties and quantitative studies on the products released during grinding still need to be done.

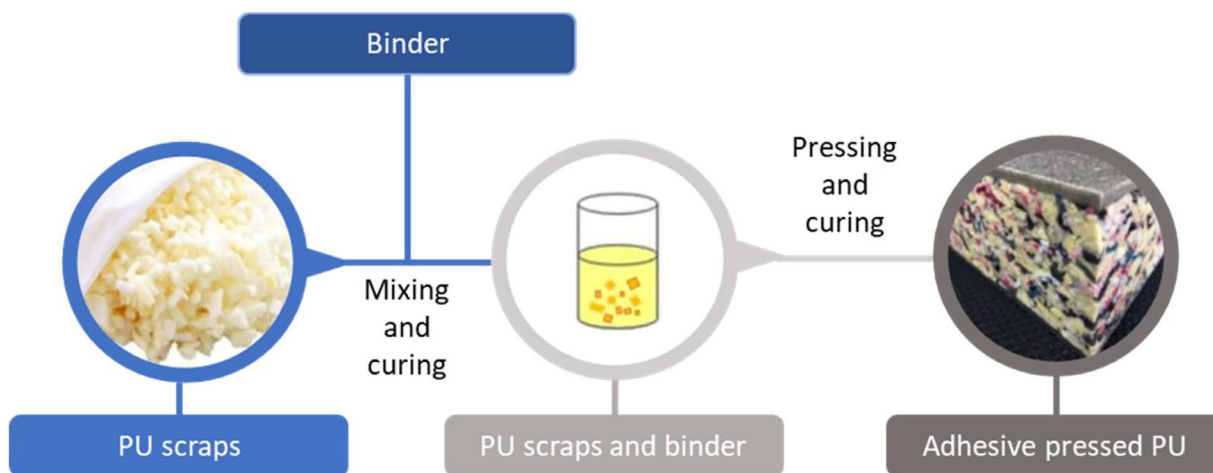
7.2.2. Re-bonding

Re-bond is a molded PU product created by combining and binding together pieces of shredded flexible PU foams. Its relative high density and excellent resilience make it suitable for various applications, including flooring or sport mats, for example. A general scheme of the re-bonding process is shown in Scheme 43.

Several parameters such as the quality and quantity of the binder, particle size and compression ratio can be carefully selected to produce materials with a wide range of applications compared to virgin materials. The process is easily scalable for industrial production, aiming to create significant quantities of new recycled materials. In fact, among all recycling techniques, re-bonding represents the largest portion of recycled PUs, with 50,000 tons processed annually in Western Europe [326]. Numerous applications have been developed and reported in the literature [327,328]. As an example, Triolo *et al.* [329] patented a filled re-bonded PU. Chopped PU particles were mixed with an inorganic mineral filler and a prepolymer binder. After adding some water to create a foam, the entire mixture was cured and compressed, re-



Scheme 43. General scheme of the re-bonding process to recycle PUs.



Scheme 44. General scheme of the adhesive pressing to recycle PU.

sulting in a filled re-bonded PU that was softer than unfilled PU foams.

7.2.3. Adhesive pressing

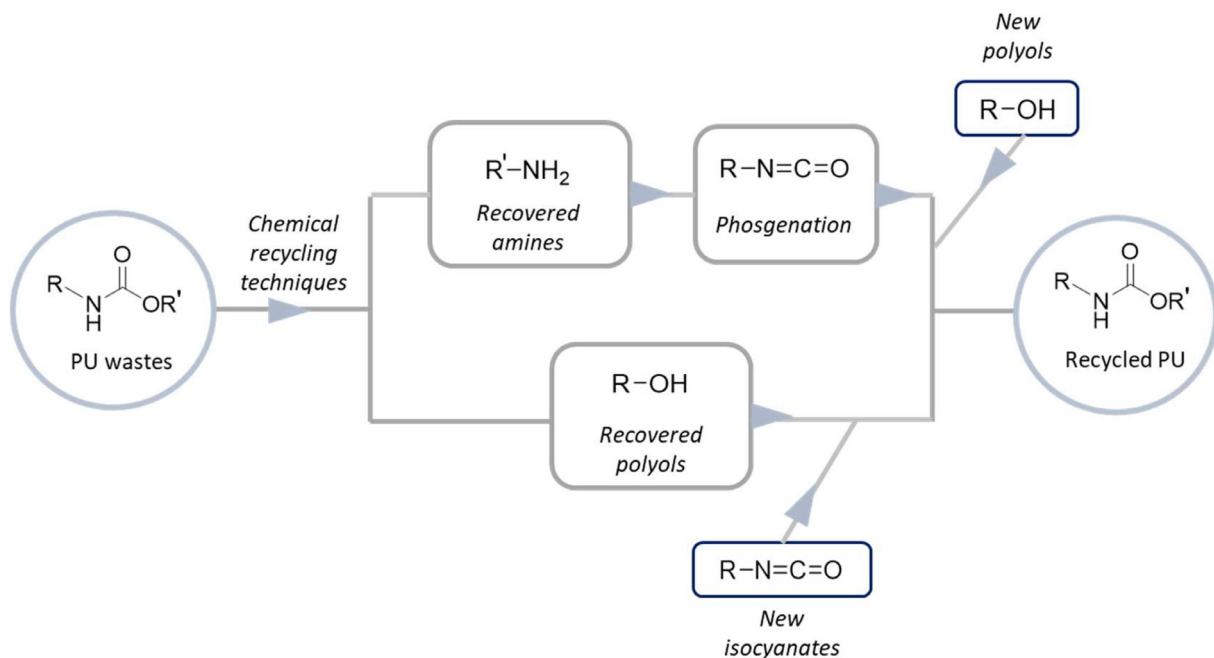
The adhesive pressing process closely resembles the re-bonding technique and has been in development for many years. A general scheme of the process is presented in Scheme 44. Adhesive pressing is carried out by blending PU waste particles (around 1 cm) with a binder and subsequently bonding them together using a thermo-press at pressures ranging from 20 to 300 bars and temperatures between 100°C and 200°C. The most important adhesive binders used for this process are di- or polyisocyanates such as MDI, TDI or polymeric MDI [330]. In the formulation of the recycled PU, the di- or polyisocyanate makes up approximately 10% of the total mixture by weight, while PU scraps constitute a range between 30 % and 70 %. This process enables a wide range of applications for recycled PU, including mats, flooring, and carpets. Different binders, such as resins, can also be utilized. Hulme *et al.* [331] reprocessed shredded PU particles through compression molding, employing a polyester resin binder. During curing at temperatures between 100°C and 200°C, the soft segments of PU scraps can exhibit a thermoplastic behavior that interacts with the

binder. Mechanical testing of the materials revealed that the inclusion of recycled PU enhanced the flexibility and toughness of the PU materials compared to compounds containing conventional mineral fillers.

Mechanical recycling methods have already been developed by chemical industries to recycle PU materials. Nevertheless, it seems that few publications have been published on PU mechanical recycling. As underlined by Gama *et al.* [50], research should focus on these methods, due to the environmental and economic opportunities they can bring. Two reasons could explain this disinterest from mechanical recycling: (i) the loss in physical properties (Young modulus, strain at break...) and (ii) the fact that this recycling method cannot be used for materials with high mechanical physical standards but is restricted to low value-added applications. Nevertheless, as mechanical recycling enables an easy scale up and processability, new methods for physically recycling materials have been explored, including self-healing polymers.

7.2.4. Covalent Adaptable Network (CANs)

New area of research is centered on the reprocessability of thermoset PUs. The main concept of this approach is either to harness the versatility of urethane bonds, enabling reversibility in the PU



Scheme 45. Chemical moieties recovered from chemical recycling techniques to recycle PUs.

structure, or to synthesize PUs containing reversible bonds. Covalent adaptable networks (CANs) are reprocessable and self-healing thermoset polymers that operate based on two mechanisms: associative or dissociative mechanisms. These mechanisms involve exchangeable bonds that allow to combine the benefits of thermoset and thermoplastic. The polymer behaves like a thermoset (insoluble, infusible) until specific stimuli (such as light, temperature or pH) trigger the rearrangement of certain bonds within the network, causing the polymer to transition to a thermoplastic state. The most studied dissociative CAN mechanism is the Diels Alder [332,333] reaction due to its thermal reversibility. However, this pericyclic reaction affects the average functionality of the network. Industrially, the most widely used reactions are condensation reactions such as transamination [334] or transesterification [335]. For polyurethane, transcarbamoylation at high temperature can lead back to isocyanate and alcohols [336]. The transcarbamoylation can also occur in NIPUs structure. Yang *et al.* [337] exhibited the self-healing ability of NIPUs. Indeed, after the polymer underwent physical or chemical treatments, they have shown that its mechanical properties were not altered. It was made possible by the bond exchange between carbamate and hydroxyl. Pronoitis *et al.* [338] included a disulfide bond in their NIPUs structure in order to facilitate the recycling by using cystamine as the amine. Thus, the exchangeable ability of the disulfide bridge and free radical reactions are examples of associative networks [339]. Some authors showed that it was possible to physically recycle PUs by using a post-synthetic carbamate bond exchange catalyst: the DBTDL [340]. Quienne *et al.* [192] highlighted that bio-based PU foams can be easily reprocessed using compression molding at 160°C for 30 minutes. As they validated the fact that foams coming from different origins can behave as a covalent adaptable network, this process can be extended to conventional PUs at industrial scales. Sheppard *et al.* [340] performed the recycling of PUs with a twin-screw extrusion at 220°C in order to efficiently remove air trapped in the PU foam structure to make films. All these physical processes are operating at high temperatures. Chemical processes can also produce CANs but typically involve lower operating temperatures. In this context, Zhao *et al.* [341] used the transurethanization to demonstrate their ability to recycle PU at low tempera-

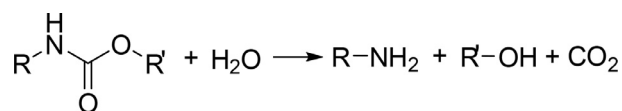
tures (below 70°C) with a soft base. They initiated the depolymerization process through methanolysis using a base catalyst. The resulting molecules are O-dimethylcarbamates and polyols. Subsequently, through polycondensation, PUs are reformed with the elimination of methanol. This method can be employed for recycling PUs or by isolating the biscarbamate and reacting it with another alcohol to create a new PU. Furthermore, according to the authors, this process is easily scalable. On the other hand, materials with special properties, such as fire retardancy can be a bottle neck for the industrialization of this process due to the strict legislation on the synthesis of plastics for application such as biomedical or food contact.

7.3. Chemical treatment

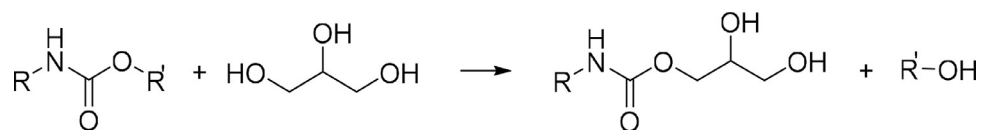
The main goal of chemical treatments is to recover monomers from the PU materials under controlled experimental conditions. The PU wastes are treated according to chemical methods such as hydrolysis, glycolysis, aminolysis or acidolysis. The main products obtained at the end of the process are amines and polyols. The chemical recycling techniques are illustrated in Scheme 45.

7.3.1. Hydrolysis

Hydrolysis is one of the oldest methods for the chemical recovery of PU foams. In hydrolysis, PU waste is exposed to a superheated water stream at 200°C and a pressure of approximately 15 atm, resulting in a two-phase liquid product containing polyols and diamines, respectively [322,342]. The upper aqueous phase contains the amines, while the lower phase consists of the recovered polyol. PUs are treated with water vapor in a reactor under high pressure and high temperatures. The general mechanism of hydrolysis is depicted in Scheme 46.



Scheme 46. Reaction scheme of urethane hydrolysis.



Scheme 47. Reaction scheme of urethane glycolysis.

The main drawback of this method is the undesired production of primary aromatic diamines: MDA or 2,4-toluylene diamines (TDA) [342,343]. These products are not only toxic but affect the quality of the recycled polyols as the viscosity of the mixture increases with the aromatic diamine content. The amines can be reused through phosgenation reaction to synthesize new isocyanates. The recovered polyols can be blended with virgin polyols, up to 20 %, in foam formulations [344]. Nevertheless, the main drawback of this method is that it requires an important energy input, harsh reaction conditions and does not suit well with a profitable post-recycling market making this method unfavorable [7].

7.3.2. Glycolysis/Alcoholysis

Glycolysis/Alcoholysis have been the most widely used and convenient method for recycling PUs since the 1980s. It involves the depolymerization of PUs using low molar mass diols, polyols or glycerol and is carried out at temperatures generally close to 200°C. The objective is to obtain a homogeneous and low-viscosity phase containing polyols with a high hydroxyl number, enabling them to react with isocyanates subsequently. Typically, the process is conducted with a significant excess of alcohols to yield two phases. The upper phase is mainly formed by the recovered polyol. The lower phase contains the by-products of side reactions and the excess of alcoholysis agent, which enables more efficient recovery of the polyol. The general reaction of the glycolysis is given in Scheme 47.

Many catalysts can be used for the depolymerization of PU by glycolysis: alkaline hydroxides, alkaline acetate, amines, organometallic compounds, and stannous compounds. The choice of the depolymerization agent and the catalyst depends on the initial PU feedstock. Wang *et al.* [345] described the glycolysis of TPU based on MDI and PEG. Diethylene glycol (DEG) and ethylene glycol (EG) were used as agents of the glycolysis and ethanolamine (EA) and lithium acetate as catalysts. The ratio that allows to separate the different products of the glycolysis is 9/9/2 for DEG/EG/EA respectively in two phases, the upper one containing polyether polyols. They managed to recover a polyol with similar properties namely hydroxyl values, molar mass and dispersity compared to the virgin one. Then, the recovered PEG can be employed to synthesize new PUs using diisocyanates.

Garmarudi *et al.* [346] experimented the depolymerization of PU flexible foams using DEG and pentaerythritol as polyols and NaOH as the catalyst. The mixture was heated at reflux for 4 hours. They found out that the best ratio of DEG/PE to separate the flexible foams from the rigid ones was 9/1.

Modesti *et al.* [347] described the glycolysis of PU flexible foams with EG operating with a foam/EG ratio of 1 at 190°C for 2 hours, resulting in two liquid phases and a solid one, with a ratio of 44: 54: 2 w/w. The upper phase mainly contained the polyether polyol and the bottom layer the aromatic products from the isocyanates, which were solubilized in EG. The solid phase was mostly composed of ureas and carbamates compounds. They highlighted that using hexamethylenetetramine enables to obtain only two liquid phases. Indeed, it reacts with amines formed in the system preventing the formation of heavy polyureas that form the solid phase. Having only two phases instead of three makes the whole recycling process easier to be set up at pilot and industrial scale.

Vanbergen *et al.* [348] described key factors to improve the split-phase alcoholysis of TDI-based flexible PU foam. 2-pyrrolidone was added to facilitate the dissolution and repolymerization process. They could obtain a high purity polyether polyol (97 %) with a 98 % yield and used it further to replace the virgin polyether polyol for up to 50% in the synthesis of PU foams with similar mechanical properties.

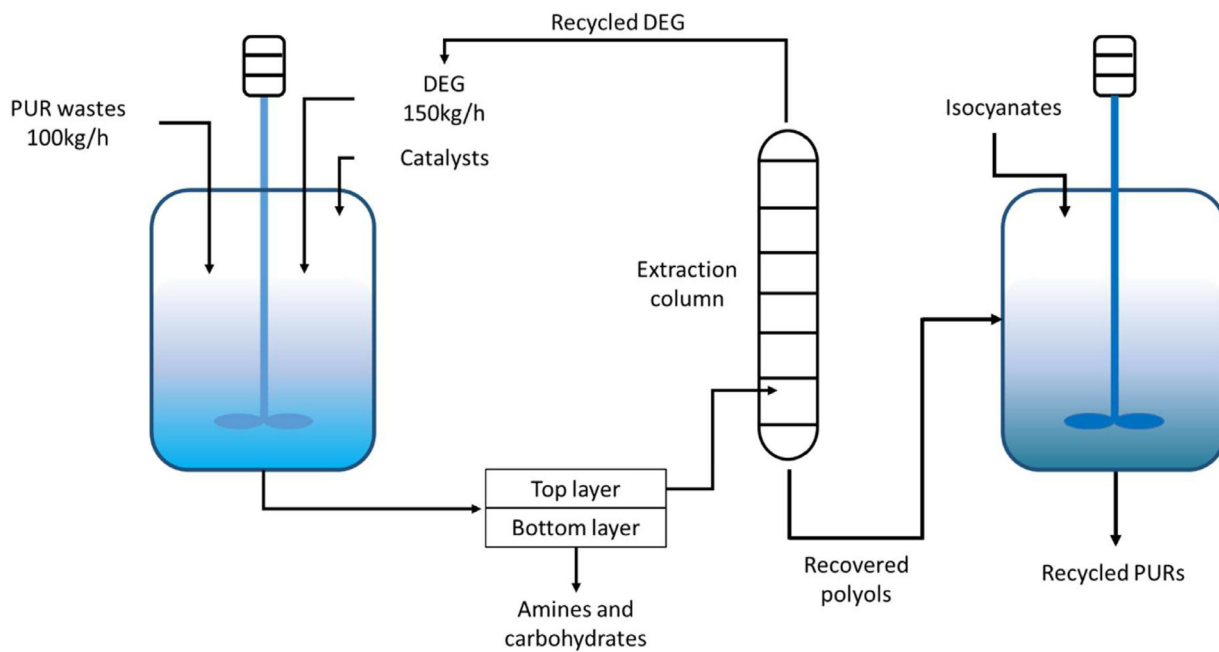
The glycolysis has been performed at different scales: laboratory and pilot plant. Huntsman corporation developed a split-phase glycolysis process at the pilot plant scale for recycling PUFs based on MDI and high molar mass polyols. A general scheme of the operation unit is given in Scheme 48.

This production unit allows recycling 100 kg of PU foams per hour using 150 kg of DEG as glycolysis agent at 200°C for 3 hours [349]. The upper phase contains the unpurified polyether polyols mixed with DEG. To recover the DEG and enhance the purity of the polyol, an extraction unit is installed, and an evaporation module has been integrated into the process to specifically recover the glycol. The bottom phase is thus mainly composed of carbamates and amines. The purified polyether polyol obtained at the end of the glycolysis process can be used as raw polyether polyol for the synthesis of new PU foams by mixing them with isocyanates like MDI or TDI. Nevertheless, the industrial scale of the split-phase glycolysis process has not been yet set up due to the important need of glycolysis agent and the contaminants coming from the PU foams that end up in the polyol phase, reducing its quality. Nevertheless, further studies on glycolysis would benefit the worldwide recycling industry of plastics from an ecological and economic point of view.

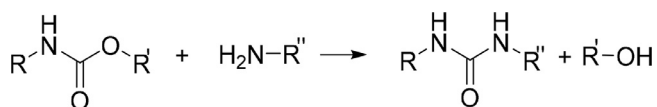
7.3.3. Aminolysis

Aminolysis is a transurethanization process that involves interchanging the ester groups of the urethane function by an amine, resulting in bi-functional compound containing a urea functionality (from an aliphatic or aromatic amine) into the structure of the PU. The reaction is carried out at 180°C for 70 minutes, as reported by Chuayjuljit *et al.* [350] The general mechanism of the aminolysis is given in Scheme 49.

During this process, two phases are obtained: the upper phase containing the unrefined polyol mixed with amines and a bottom phase mostly composed of TDA. The recovered unrefined polyol can be used to synthesize new PU up to 80 %. However, by purifying the upper phase through distillation with the aim of removing amines, new PU can be synthesized using 100 % of the recovered refined polyol. The reaction rate can be enhanced by adding catalysts at the beginning of the depolymerization process. It has been reported that the reaction rate is more efficient when stronger bases are used as catalysts. Consequently, amines such as diethylene triamine (DETA) or triethylenetetramine (TETA) are commonly employed to catalyze the depolymerization of PU. DETA is a more effective depolymerization agent than TETA, which, in turn, is a more effective aminolysis agent than TEPA [351]. It has also been reported that aminolysis can be catalyzed by metal oxides such as potassium oxides. Chuayjuljit *et al.* [350] conducted experiments to catalyze the depolymerization of PU foams with NaOH using DETA as a degrading agent. As they increased the amount of NaOH, the reaction rate improved. This led to a reduction in the viscosity of the two liquid phases, resulting in better recovery of the refined polyol. However, it's worth noting that this method of recycling PU



Scheme 48. General scheme of the glycolysis process developed by Huntsman.



Scheme 49. Reaction scheme of urethane aminolysis.

waste has not been scaled beyond the laboratory, as reported by Simón *et al.* [352].

7.3.4. Acidolysis

As recently reported by Gama *et al.*, acidolysis represents another alternative to recover the polyol from PU scraps [353]. The goal is to optimize and adjust reaction parameters to obtain a certain type and quantity of polyols directly for the desired application. The general mechanism of the acidolysis is given Scheme 50.

Several dicarboxylic acids can be employed in the acidolysis of PUs scraps, including oxalic acid, malonic acid, succinic acid, or adipic acid as reported by Godinho *et al.* [354]. As mentioned earlier in the Section 3.1.1. about bio-based polyols, these acids are entirely derived from renewable sources, which has positive implications for environmental impact across various LCA categories.

Lower temperatures and shorter reaction times lead to a final product with a higher acid value, lower hydroxyl value, greater molar mass, and increased viscosity. In contrast, higher temperatures and longer reaction times result in a polyol with a lower acid value, higher hydroxyl value, lower molar mass, and reduced viscosity [354]. Grdadolnik *et al.* [355] attempted several conditions with higher temperatures than conventional ones (230°C compared to 180°C) and managed to drastically reduce reaction time (less than one hour) compared to acidolysis conducted at conventional

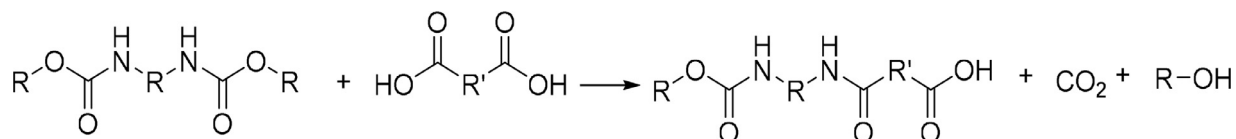
temperatures (at least six hours). They also demonstrated that the quality of the recovered polyol remained unaltered. However, unlike glycolysis, acidolysis does not allow the complete recovery of a functionalized polyol that perfectly matches the original one. This limitation arises from esterification, which occurs as a side reaction, resulting in polyols terminated with carboxylic acid groups.

Some drawbacks of the chemical methods for recycling PU foams, which hinder their scaling up at the industrial level, include: (i) they are highly energy-intensive processes, requiring high temperatures of around 200°C for at least one hour, and (ii) the primary products obtained are the recovered polyol, as well as small oligomers whose nature depends on the specific method employed, such as MDA, TDA, or amines, for example.

Subsequently, the recovered polyols must undergo purification to achieve material with the desired physical and mechanical properties. Moreover, separating the polyol from other products helps reducing the viscosity of the liquid phase containing the refined polyol, making the purification process more manageable. However, this purification step is typically too complex to implement, which remains a barrier to the industrial-scale development of these recycling techniques. Despite all these barriers, PU chemical recycling is becoming an industrial reality as exemplified by the Renuva™ mattress recycling program launched by Dow Chemicals and that aims at recovering polyols from discarded mattresses made of PUFs [356].

7.4. Enzymatic PU degradation

The recent publications on PU end-of-life management are focusing on enzymatic treatments to recycle PU materials [357–359]. Despite chemical recycling enable the recovery of certain



Scheme 50. Reaction scheme of urethane acidolysis.

molecules that can serve as feedstocks for PU materials, the quality and wide range of recovered polyols and amines make this recycling method unfeasible on an industrial scale. Using enzymes to cleave urethane and ester functions allows for a more precise recovery of desired products from the PU recycling process. PU enzymatic degradation aims to break down the polymer matrix into smaller building blocks through the action of microorganisms or specific enzymes. Microorganism populations can colonize the material's surface, forming a biofilm and producing enzymes that depolymerize the polymer. Microorganisms involved in biodeterioration are very diverse: bacteria, protozoa, algae, fungi and *lichenaceae* groups [303]. Magnin *et al.* [360] described and reported several bacteria, fungi, and enzymes for their ability to depolymerize PU materials and their associated PU substrates. The most common enzymatic PU degradation mechanism involves esterases catalyzing the hydrolysis of the polyester functions in polyester-based PU. This enzymatic action results in the release of an alcohol and a carboxylic acid. Hydrolysis enzymes responsible for breaking down ester bonds, as reported in the literature, include lipases [361] and cutinases [362,363]. However, it has been noted that esterases are not specific to urethane bonds, as they can also cleave ester bonds. New enzymes have garnered attention for their specific degradation of PU bonds: amidases and proteases. These enzymes are known for cleaving peptides, but several authors have demonstrated that they can also hydrolyze urethane bonds, releasing an amine, an alcohol, and a carboxylic acid [363,364].

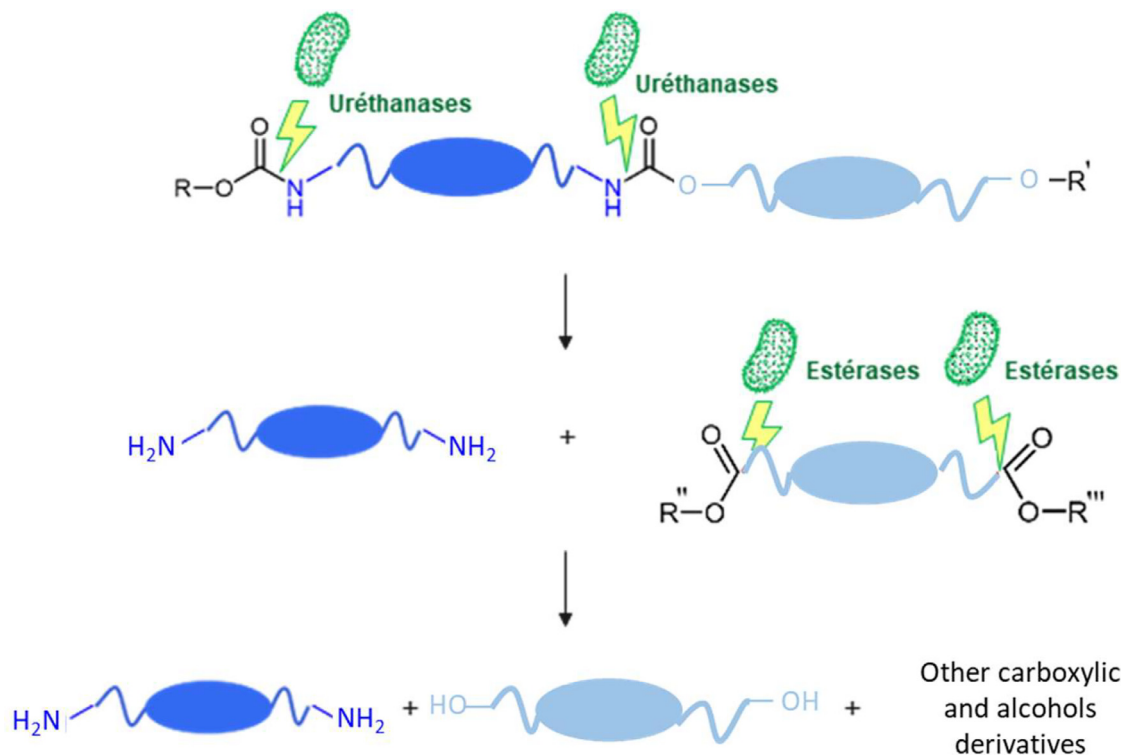
While proteases and amidases drew attention for hydrolyzing urethane bonds in PUs, the processes are extremely slow and minimal degradation is achieved even after several months [365,366]. Nevertheless, Branson *et al.* [366] have recently reported the discovery of urethanases from soil exposed to PU waste for many years that are able to convert dicarbamates into alcohols and amines in only few hours. A two steps process was thus developed with the polyether-PU foam being converted into low molar mass dicarbamates by chemical glycolysis, and then hydrolyzed in the

presence of the enzymes to finally recover the polyether-polyols and the aromatic diamines.

Nevertheless, PU materials often prove recalcitrant to biodegradation when exposed to bacteria, fungi or enzymes [358]. Oprea *et al.* [367] explained this recalcitrance by the segmented nature of PU morphology, consisting of hard and soft segments. They studied the degradation of PEG-based polyurethane elastomers with different ratios of hard segments using a soft rot fungus *Chaetomium globosum*. Their findings indicated that the higher the proportion of hard segments in the PU, the less efficient the degradation process became [367]. This recalcitrance can also be due to the presence of additives in PU materials.

To address this degradation issue, various solutions have been explored in the literature. One emerging strategy involves the discovery of new PU depolymerization enzymes using metagenomics tools to identify and isolate them from microbial communities. In this way, Ng *et al.* [368] studied the in vitro enzymatic degradation of PU modified with palm oil-based polyester polyol. They observed a significant weight loss (90 %) of the material after 28 days. However, PU enzymatic hydrolysis in this case was made possible because PEG was used as the polyol in the PU formulation. This soft segment introduced sufficient hydrophilicity and water absorption into the material, enabling the action of lipase. Another strategy to consider is investigating the impact of a mixture of multiple enzymes that could work synergistically to efficiently depolymerize PU materials [365]. Cregut *et al.* [303] proposed a model of PU degradation illustrated in Scheme 51.

Indeed, the greater the diversity of these communities, the more efficient biodeterioration becomes. This is primarily due to the different microorganisms that can organize themselves, generating nutrients from depolymerized monomers and functioning symbiotically [369]. To achieve effective biological recycling of PUs, it is crucial to control the structure of recovered products and convert them into valuable building blocks for second-generation PU materials. To date, the easiest way to confirm urethane bond hydrolysis is by detecting amines directly derived from PU degrada-



Scheme 51. A model of enzymatic depolymerization proposed by Cregut *et al.* [303], Copyright 2023. Reproduced with permission from Elsevier.

tion. The economic potential that enzymatic degradation holds for advancing a circular economy for PU materials is underscored by Uekert *et al.* [370] in a recent publication describing the LCA of the enzymatic PET recycling. They were the first to model an enzymatic recycling process for a plastic. It would be highly interesting to build upon this study conducted on PET and apply it to PUs. Indeed, this study allowed for the modeling of the entire PET recycling process and the operational units that could be established to maximize yield at all stages. They initially introduced a mechanical recycling method involving the grinding of PET materials, followed by enzymatic PET depolymerization. To minimize energy costs, a membrane system is used for sorting recovered products instead of relying on distillation. Currently, LCA indicates that recycled PET still lags behind virgin PET in terms of performance, but there are opportunities for improvement in waste stream reduction, enhanced mechanical pretreatment, the use of sodium hydroxide in the process, and improving the yield of converting PU flakes into valuable products. Nonetheless, significant opportunities for research and innovation exist to advance polymer circularity and make it feasible at an industrial scale.

Despite efforts aimed at improving PU recycling efficiency, too few PU materials are currently recycled or have a proper end-of-life plan. Zhang *et al.* [371] highlighted the significant sorption of microplastics by PUs in the environment, including aromatic compounds and their derivatives. From this perspective, the end-of-life of PUs should be the foremost consideration and subject of in-depth investigation prior to their synthesis and property development. The majority of PU developed in industries are not designed with a proper end-of-life considerations, which complicates any subsequent valuable recycling efforts. Kaur *et al.* [19] emphasized that using modified building blocks during the formulation and synthesis of new polymers represents a step toward genuine sustainability for PU materials. Biodegradation could then become more attainable and help address PU waste issues. PU formulation would thus transition from being toxic and hazardous to eco-friendly and sustainable.

8. Conclusions and Outlook

PUs, ranked amongst the 6th most produced polymer in the world, are continuously raising attention towards their toxicity, origin, sustainability, recyclability and end-of-life. To overcome isocyanate toxicity, some actions were already taken. Nowadays, isocyanate producers know perfectly how to deal safely with phosgene and control risks of toxic gas leakage at an industrial scale. Some isocyanates are highly toxic; explaining why low volatile isocyanates are preferably used. Blocked isocyanates and WPU systems were created to avoid isocyanate handling risks. Moreover, bio-based polyfunctional short alcohols were designed to propose greener PU materials. This new proposal grew quickly in popularity. Consequently, bio-based polyfunctional alcohols were proposed by both academia and industry to widen the scope of available bio-based polyols. Very recently, new structures of bio-based di- and polyfunctional isocyanates have emerged, allowing to design fully bio-based PU materials. Despite the progress about bio-based polyisocyanates, some questions about sustainability of raw material origin can be highlighted. For example, should we grow agricultural land and feedstocks for chemical industry or is it better to use them for food consumption? Should we synthesize compounds derived from palm oil while palm oil exploitation is responsible of deforestation?

NIPUs could be an answer to reduce isocyanate toxicity and PUs environmental impact. Among NIPU systems, PHUs are the most promising since they can be obtained from CO₂ and bio-based chemicals. However, those systems require high temperature and very long reaction times due to their low reactivity, limiting

their industrial application. By shortening reaction times, avoiding the use of solvents and efficiently mixing high viscosity formulations, mechanochemical processes (ball-milling, reactive extrusion or reaction-injection molding) could answer to PU sustainability questions. Nevertheless, at the end of their lives, PU must be eliminated. Only 5 % of PU wastes are recycled compared to 50 % and 45 % of PU wastes that are respectively landfilled and burnt. Even if more sustainable PU materials can be synthesized, they still contain urethane backbone which must be destroyed. A way to lower the environmental impact of PUs is to extend their life cycles by recycling or reusing them. Recycling conventional PUs can be difficult for different reasons. That is why it is in our shared interest to tailor PU by looking at the targeted recycling method. Usually, we attempt to synthesize PU materials to follow the defined features. Instead, it could be a good option to first think about the recycling way of the final product at the end of its life and then try to build a material that respect both defined physical, mechanical, thermic features and a sustainable recycling route.

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.

CRediT authorship contribution statement

Aliénor Delavarde: Writing – original draft. **Gaëlle Savin:** Writing – original draft. **Paul Derkenne:** Writing – original draft, Conceptualization. **Marine Boursier:** Writing – original draft. **Roberto Morales-Cerrada:** Writing – original draft. **Benjamin Nottelet:** Writing – review & editing. **Julien Pinaud:** Writing – review & editing. **Sylvain Caillot:** Writing – review & editing, Conceptualization.

Data availability

No data was used for the research described in the article.

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