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Beyond the polyol: valorization of the derivatized isocyanate fraction after chemical recycling of polyurethane

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This review is the first to address the fate of the isocyanate-derived fraction resulting from polyurethane (PU) chemical recycling. While most literature focuses on polyol recovery, this work highlights valorization strategies for the underexplored isocyanate-derived fraction obtained *via* glycolysis, aminolysis, phospholorysis, alcoholysis, *etc.* While many valorization routes face technical or economic barriers, several show industrial promise. Pathways such as poly(urethane-urea) synthesis *via* hindered urea bonds, alkoxylation to rigid polyols, and thermolysis of carbamates offer circularity and energy efficiency, though safety and regulatory constraints, limit scalability. Other routes, including epoxy curing and polyamide synthesis, balance recyclability, cost, and complexity. A case-specific evaluation remains essential to identify viable strategies for sustainable PU valorization.

Sustainability spotlight

The large-scale production and disposal of polyurethanes constitute a growing environmental challenge due to their high volumes, complex chemical structures, and limited high-value recycling routes. Addressing this issue is essential, as conventional end-of-life treatments rarely preserve the chemical value of these materials, thereby hindering true circularity. The sustainable advance of this work lies in its focus on the valorization of derivatize disocyanate fractions, emphasizing the recovery and reintegration of chemical building blocks into new materials while minimizing the use of hazardous reagents in line with green chemistry principles. By moving beyond depolymerization toward functional reuse of recycled intermediates, this work supports circular material pathways and aligns with UN SDGs 9 (Industry, Innovation and Infrastructure), 12 (Responsible Consumption and Production), and 13 (Climate Action).

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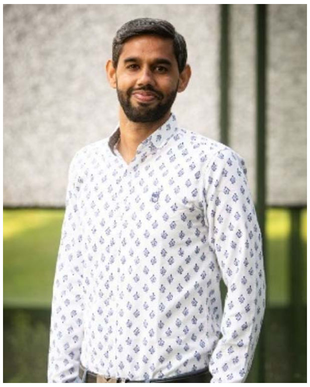
Introduction

Polyurethane (PU) was invented in 1937 by Otto Bayer. Since then, the popularity of this polymer has grown substantially, and PU materials have become an integral part of everyday life. They are widely used in insulation for refrigerators and freezers, building materials, mattresses, cushions in furniture and automobiles, and many other applications. This broad applicability stems from the diverse building blocks that can be employed in PU synthesis (Table 1). PU is composed of two primary monomers: polyols and isocyanates. When isocyanates are combined with long-chain polyols, the resulting PU is flexible and commonly used in products such as mattresses and car seat cushions. Conversely, the use of isocyanates with low molecular weight polyols yields a rigid PU, primarily applied in insulation materials. The most commonly used polyols in PU production are polyether polyols and polyester polyols. Polyether polyols are typically synthesized *via* polymerization of propylene oxide (PO) or ethylene oxide (EO), and are favored in applications where cost-efficiency, flexibility, and hydrolytic stability are essential. In contrast, polyester polyols are produced through co-polymerization of polycarboxylic acids (or anhydrides) with polyhydric alcohols (glycols), and are valued for their high mechanical strength and thermal stability. The predominant isocyanates used in PU synthesis are the aromatic compounds toluene di-isocyanate (TDI) and methylene diphenyl di-isocyanate (MDI), including their isomeric forms. Additionally, a polymeric variant of MDI, known as polymeric methylene di-isocyanate (PMDI), is frequently utilized. PMDI remains liquid at room temperature, making it more suitable for foam production due to its ease of handling compared to solid MDI.

The versatility of PU and its constituent monomers is reflected in the wide array of applications, which can be broadly divided into two main categories: foams and CASE materials (coatings, adhesives, sealants, and elastomers). Among these, PU foams dominate the market, representing approximately two-thirds of all PU-based products.[2]

PU foams are produced by mixing polyols and isocyanates in the presence of various additives, including surfactants, catalysts, flame retardants, and, crucially, a blowing agent. Mixing these different components not only results in the formation of urethane compounds but also a whole range of by-products (Scheme 1). Water is most commonly used as a blowing agent, as it reacts with isocyanates to form carbamic acid, which subsequently decomposes into an amine and carbon dioxide (CO_2). The released CO_2 gas drives foam formation, while the resulting amine further reacts with isocyanates to form urea



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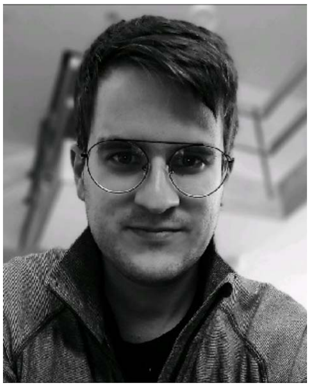

Pieter Billen

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Table 1 Overview of different types of PU and their monomers[1]

	Flexible PU	Rigid PU	CASE/TPU
Applications	Mattresses Automotive (seats) Furniture Packaging inlays	Appliance insulation Automotive Spray foams	Coatings Adhesives Packaging (films) Elastomers (electronics wearables) Sealants
Main polyols	Mainly EO/PO MW > 3000; $f = [2.5\text{–}3]$	Mainly PO	TTMEG/PEG polyethylene adipate polybutylene adipate polycaprolactone acryllic/polycarbonate tailored to application
Main isocyanates	2,4-TDI, 2,6-TDI	pMDI	HDI, IPDI, H_{12}MDI, CHDI

linkages that become an integral part of the PU foam structure. In addition to urea linkages, PU foams may also incorporate isocyanurate and uretdione linkages, depending on the formulation and processing conditions.[3] These structures arise from the high reactivity of isocyanates, which are capable of undergoing self-condensation. Among them, isocyanurate linkages are particularly noteworthy due to their excellent thermal stability, which significantly enhances the overall heat resistance of PU materials.

The majority of PU produced are thermosets, a property that contributes to their exceptional durability. A clear example of this longevity can be found in the construction sector, where PU insulation materials often remain effective for over 50 years. Given both the high production volume and extended lifespan of PU products, the development of sustainable end-of-life treatment strategies is becoming increasingly important. At present, most post-consumer PU waste is either sent to landfills or utilized for energy recovery.[2]

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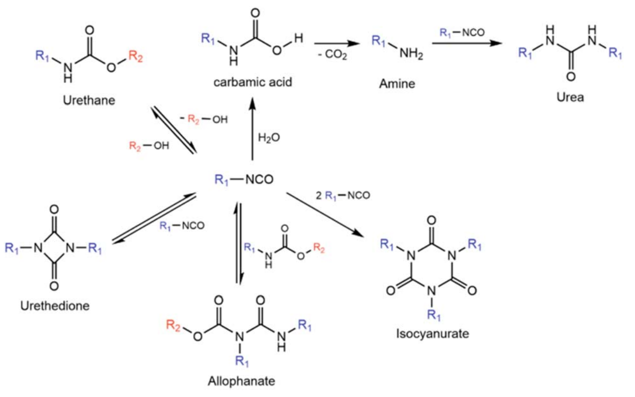


Scheme 1 Reaction and side reactions during the formation of polyurethane foam.

Several recycling methodologies have been developed for polyurethane. The first is mechanical recycling, in which PU is physically fragmented into smaller pieces, subsequently washed and reassembled, typically using an isocyanate-based adhesive. This process leads to increased foam density and heterogeneity, along with altered mechanical properties. Ironically, the same characteristics that make PU a durable network polymer also hinder its recyclability, as thermoset PU cannot be remelted. As a result, the quality of mechanically recycled products is often inferior, contributing to market saturation and limiting the overall circularity of this method.

An alternative approach is thermochemical recycling, which aims to break the urethane bonds through thermal treatment.[4] This recycling method presents several challenges. At the high temperatures typically ranging from 300 °C to 800 °C, not only the targeted urethane bonds but also other chemical bonds are broken. As a result, the process yields only short, functionalized molecules, such as alkanes, alkenes, aromatics, and oxygen- or nitrogen-containing compounds, while up to 50% of the PU mass is lost as char.[5] This process is also highly energy-intensive, as it requires elevated temperatures, an inert atmosphere, and extensive separation steps to isolate the various end products.

A third methodology is chemical and biochemical recycling, which employs chemical agents, microorganisms, or isolated enzymes to break down the polymer structure.[6] The products of this recycling method are polyols and derivatized isocyanates. Among all available techniques, chemical recycling appears to be the most promising in terms of circularity, as it enables the breakdown of PU into valuable building blocks. While several chemical recycling approaches can efficiently regenerate polyols, the same does not apply to isocyanates. This imbalance primarily arises from the fact that polyols can be recovered in their original form, whereas isocyanates undergo derivatization during chemical recycling, resulting in compounds such as amines, carbamates, and ureas. These derivatized functionalities exhibit reduced reactivity compared to native isocyanates, diminishing their thermodynamic relevance. Additionally, mixtures of various derivatized isocyanate fractions may be present in the recycling output due to the diversity of chemical bonds in PU, such as ureas, isocyanurates, and uretdiones.

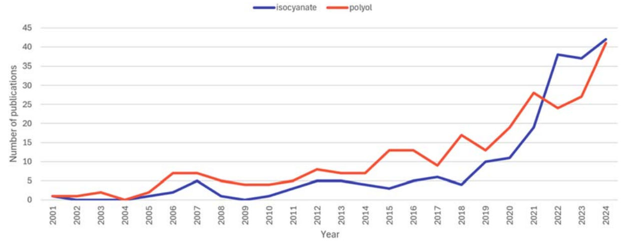


Fig. 1 Number of peer reviewed publications (from 2001 to 2024) on the subject of polyurethane recycling and (1) blue graph: isocyanates (2) red graph: polyols. Data acquired through Web of Science on 10th of July 2025.

These bonds yield different end products upon chemical recycling, which must be considered when valorizing the final mixture. As a result, these derivatized isocyanates are generally unsuitable for direct use in PU synthesis and are often treated as waste or impurities within the recovered polyol phase. Although interest in this fraction has grown in recent years, it is now widely acknowledged that industrializing PU recycling requires addressing the isocyanate fraction, which constitutes approximately 20–65% of the total PU mass.

Fig. 1 provides an overview of peer-reviewed publications on polyurethane recycling, comparing the focus on polyol recovery *versus* isocyanate recovery. The figure clearly illustrates the historical knowledge gap between these two areas, as well as the recent progress made toward bridging it.

This review primarily focuses on the valorization of the isocyanate-derived fraction, as this topic has thus far remained largely underexplored. In contrast, the general recycling strategies for PU have already been extensively reviewed in the literature and will therefore only be addressed briefly, with attention limited to the most established chemical recycling methods. This focus is further justified by the fact that emerging chemical recycling technologies almost invariably generate the same isocyanate-derived fraction. As a result, the subsequent valorization pathways discussed here are not only relevant for conventional recycling routes but can also be directly applied to the products obtained from these newer processes. In doing so, it is the first to emphasize that the choice of chemical cleaving agent is not only critical for the depolymerization step itself, but also determines the broader potential for valorizing PU after recycling.

While certain cleaving agents may yield high depolymerization efficiency, they can simultaneously render the resulting isocyanate-derived fraction dependent on multiple energy-intensive transformations before it can be reintegrated into PU synthesis or alternative applications. This directly affects the overall circularity, energy efficiency, and industrial viability of the chemical recycling process.

Chemical recycling methods for PU and the fate of the isocyanates fraction

First, the main chemical recycling techniques for polyurethane (PU) are reviewed, with particular emphasis on the derivatized isocyanate fraction. As mentioned earlier, and as illustrated in Fig. 2, the composition of this fraction will vary depending on the cleaving agent used.

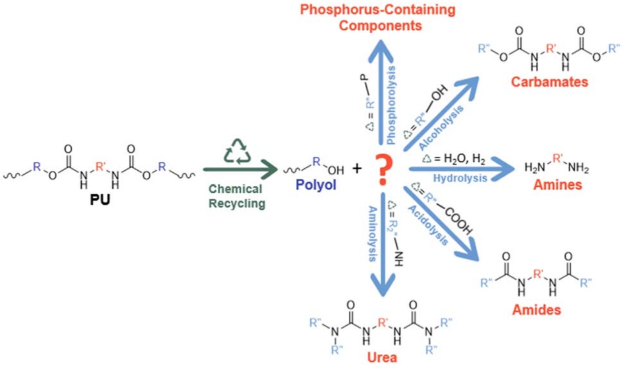
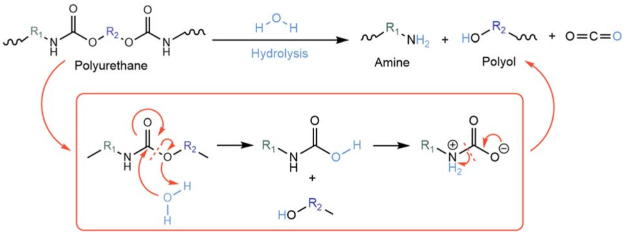


Fig. 2 Overview of chemical recycling techniques of PU and the corresponding end products.



Scheme 2 Hydrolysis of polyurethane, mechanism and theoretical end products.

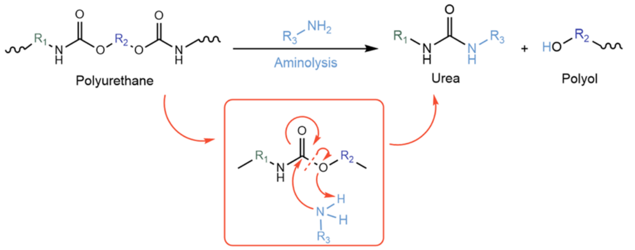
Hydrolysis

In the 1960s, hydrolysis was developed as one of the first chemical recycling techniques for flexible PU foams.[7] This process employs water or steam under high pressure (15 to 50 atm) and elevated temperatures (typically ranging from approximately 200 °C to 400 °C) to cleave the urethane bonds. This reaction yields polyols and a highly unstable carbamic acid, which rapidly decomposes into an amine and carbon dioxide (CO_2) (Scheme 2). The reaction can be catalyzed by the addition of either an acid, such as hydrochloric acid, or a base, such as sodium hydroxide.[8,9]

The polyols isolated after hydrolysis can be blended with virgin-grade polyols and used in the production of new PU materials.[10] While this technique has progressed to the pilot-plant stage, further commercialization remains out of reach due to the high energy demand of the process.

Catalytic hydrogenation

Catalytic hydrogenation is a relatively recent chemical recycling technique in which hydrogen gas, in the presence of a transition-metal catalyst, depolymerizes PU into polyols and amines.[11] Notable examples include the work of Zubar *et al.*, who reported the hydrogenation of commercial polyurethane using manganese-based catalysts under 60 bar of H_2 at 200 °C in a THF/toluene solvent system, with KO*t*Bu as co-catalyst, achieving polyol yields of up to 90%.[12] Similarly, Gausas *et al.*



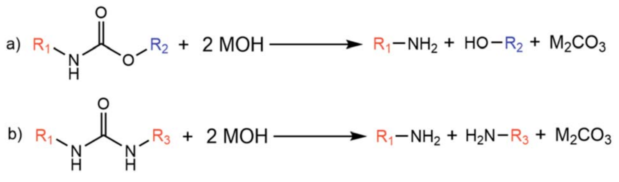
Scheme 3 Aminolysis of polyurethane, mechanism and theoretical end products.

obtained a 90% yield of amines and polyols from end-of-life flexible PU under milder conditions, 30 bar H_2 at 150 °C in isopropanol.[13] This method has attracted considerable interest due to its ability to minimize byproduct formation while enabling high recovery rates of polyols and amines from flexible PU foams, even under relatively mild reaction conditions.[13] However, yields are significantly lower for rigid foams, with only 24% of diamines recovered, owing to incomplete depolymerization of the more crosslinked PU structure.[2,13] A major limitation of this recycling approach is the high cost of the catalyst, which poses a barrier to large-scale implementation.

Aminolysis

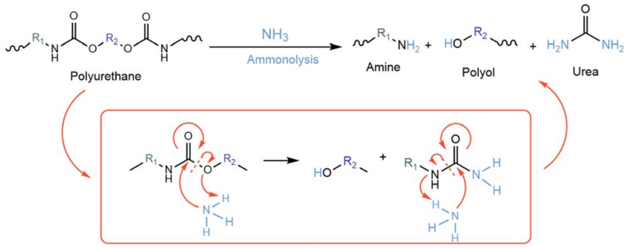
Aminolysis is one of the few chemical recycling techniques for PU that has been tested at an industrial scale to produce polyols and ureas[10] (Scheme 3). In this process, amines act as cleaving agents to break urethane bonds, resulting in a mixture of polyols and ureas. The reaction can proceed at relatively low temperatures (80 °C to 190 °C) and is catalyzed by basic compounds such as NaOH, $Al(OH)_3$, and sodium methoxide. A wide range of amines can be employed, including aliphatic and aromatic amines, alkanolamines, and polyamines.[14–16]

A critical side reaction in aminolysis is the formation of additional amines, which must be carefully considered. The extent of this reaction depends on the specific aminolysis conditions and the type of amine used. Urea bonds formed during the process are thermally unstable and tend to dissociate at elevated temperatures, producing amines and isocyanates. Kanaya *et al.*[15] demonstrated that aminolysis with alkanolamines at 150 °C yields a biphasic mixture, with the upper layer containing polyols and the lower layer primarily composed of methylenedianiline (MDA). Furthermore, it has been observed that using only a metal hydroxide catalyst significantly increases the amine content in the final product. This is because metal hydroxides promote the cleavage of both urethane and urea linkages, thereby enhancing amine formation[10] (see Scheme 4a and b).



Scheme 4 Cleavage of the urethane (a) and urea (b) bond by the metal hydroxide catalyst to form amines.

Conversely, Olazabal *et al.*[17] reported that aminolysis using a complex secondary amine (methylamino) in combination with an organic base or acid catalyst at 160–190 °C for 7 h resulted in a reaction mixture containing only polyols and diurea, with no detectable amines.



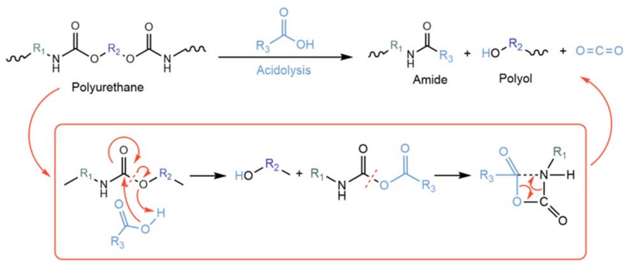
Scheme 5 Ammonolysis of polyurethane, mechanism and theoretical end products.

Ammonolysis

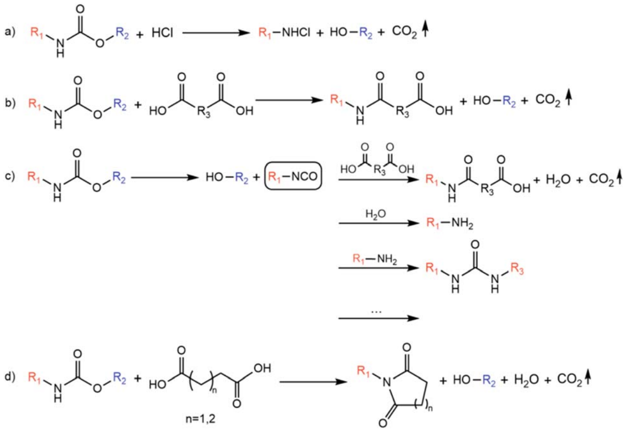
When ammonia or ammonium hydroxide is used in place of conventional amines, the process is referred to as ammonolysis. This recycling method yields polyols, amines, and urea derivatives (Scheme 5). Recently, Van Belleghem *et al.* reported the successful recycling of rigid end-of-life refrigerator PU *via* ammonolysis using NH_3 at 180 °C for 3 hours, followed by sequential EtOAc/water liquid–liquid extraction. This approach resulted in polyol yields of 73–80% with purities exceeding 97%, and amine yields of up to 95% with purities above 85%.[18]

Acidolysis

One of the most advanced chemical recycling techniques developed in recent years is acidolysis. In this process, an acid is used to cleave urethane bonds, resulting in the formation of polyols, carbon dioxide (CO_2), and a derivatized isocyanate fraction, whose composition depends on the specific acid employed.[19] Acidolysis reactions typically proceed without the need for a catalyst; however, some catalysts mentioned in the patent literature include $AlCl_3$, ZrO_2, WO_3, and WO_3–ZrO_2.[20] Both organic and inorganic acids can be employed in acidolysis. However, in the vast majority of cases, organic acids are employed (Scheme 6).



Scheme 6 Acidolysis of polyurethane, mechanism and theoretical end products.



Scheme 7 (a) Acidolysis of PU with HCl (b) acidolysis of PU with DCA (c) degradation reaction of PU and isocyanate side reactions (d) acidolysis of PU with DCAs with a short aliphatic chain.

Inorganic acids, such as hydrochloric acid (HCl), promote the formation of amine salts, whereas organic acids, such as dicarboxylic acids (DCA), lead to the formation of amides (see Scheme 7a and b). The reaction temperature is largely determined by the type of acid used. For instance, HCl-mediated acidolysis can proceed at temperatures as low as 60 °C, while DCA-based acidolysis typically requires temperatures around 200 °C.[21,22] A drawback of the elevated temperatures required in DCA-mediated acidolysis is the thermal degradation of PU, which leads to the formation of isocyanates. These isocyanates subsequently react with DCA to produce water, carboxylic amides, and carbon dioxide (CO_2) (Scheme 7c), this wide variety of end products further complicates the final reaction mixture and its consecutive separation. Although thermal degradation typically occurs around 250 °C, literature indicates that this threshold can be lowered in the presence of DCA.[22] When DCAs with short aliphatic chains are used, cyclic imides can also be formed[23,24] (Scheme 7d).

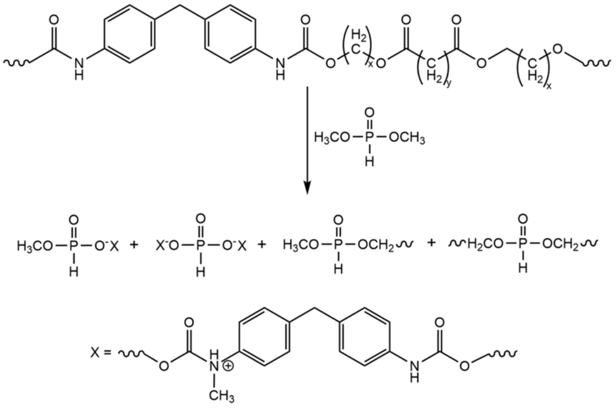
Acidolysis is the second most developed chemical recycling technique and has already been tested at an industrial scale by H&S Anlagentechnik for post production waste.[25]

Phosphorolysis

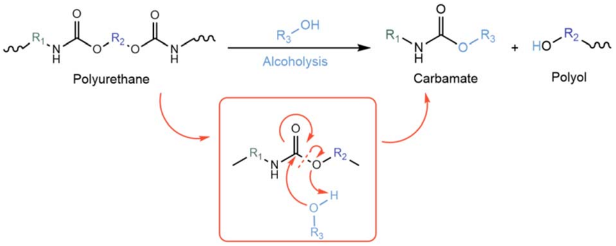
In phosphorolysis, an ester of phosphonic or phosphoric acid is used to cleave urethane bonds, resulting in polyols bearing phosphate group functionalities and phosphorus-containing isocyanate-derived compounds. An example of the phosphorolysis reaction of PU elastomer with dimethyl H-phosphonate is shown in Scheme 8. Research into phosphorolysis has been primarily conducted by Troev and co-workers; however, the method remains at the experimental stage, and no recent studies have been published on this chemical recycling approach.[25–30]

Alcoholysis/glycolysis

Among the various chemical recycling techniques, alcoholysis of PU is one of the most well-known and widely applied methods. This process typically involves the use of polyfunctional alcohols in a transcarbamation reaction, yielding polyols and carbamates as the main products (Scheme 9). When alcoholysis is carried out with an alcohol containing more than one hydroxyl group, the process is referred to as glycolysis. Notably, glycolysis is the only chemical recycling method that has been implemented at an industrial scale.[10]



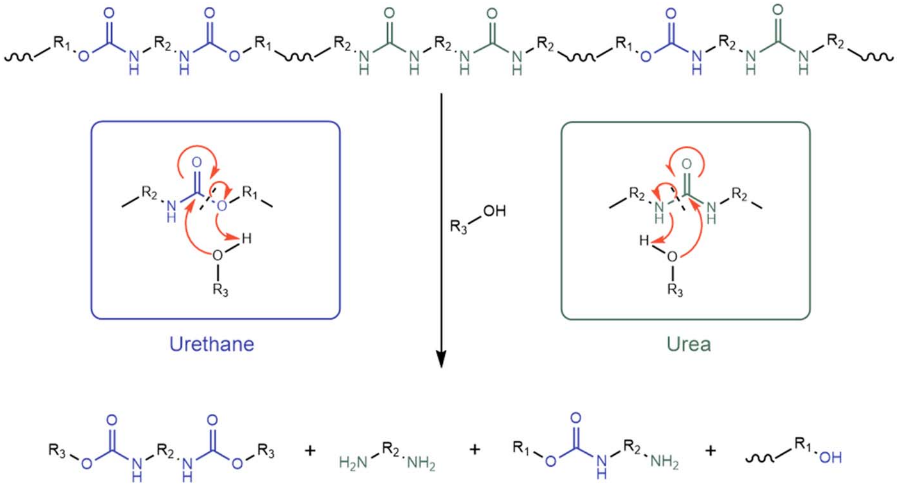
Scheme 8 Phosphorolysis of microporous PU elastomers with dimethyl H-phosphonate based on Mitova *et al.*[31]



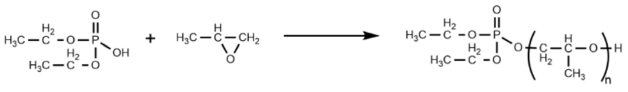
Scheme 9 Alcoholysis of polyurethane, mechanism and theoretical end products.

Early studies on flexible PU foams indicate that using a high excess of glycolysis agent, typically 1.5 kg per kg of PU, results in a biphasic mixture.[32] The upper, nonpolar phase consists of polyols formed through transcarbamation during glycolysis, while the lower, polar phase contains a mixture of the glycolysis agent, carbamates, amines, and other side products. This split-phase approach offers a significant advantage by simplifying product separation, thereby enhancing the value of the recycled output streams and increasing the proportion of recycled content that can be reused in the synthesis of new PU foams.[33]

A key side reaction during alcoholysis is the formation of amines, which occurs when alcohols react with urea linkages present in PU foams. These linkages originate from the foaming process, meaning that the amine content in the reaction mixture is directly influenced by the type and amount of blowing agent used during foam production (see Scheme 10). Importantly, this urea recycling reaction can also occur in any of the previously discussed chemical recycling methods, but this is not always considered disadvantageous, depending on the specific chemical recycling method.



Scheme 10 Cleavage of the urethane and urea bond during the alcoholysis reaction to form carbamates, amines, carbamate-amine compounds and polyols.[1]



Scheme 11 Reaction of diethyl phosphate with propylene oxide.

Hydroglycolysis

Hydroglycolysis is often described in the literature as an enhanced variant of the hydrolysis process, utilizing a combination of water and glycol to break down PU under milder conditions (approximately 160 °C).[34] During this reaction, both hydrolysis and glycolysis occur simultaneously, resulting in the formation of polyols, primarily amines, and a limited number of byproducts such as carbamates. Some studies regard hydroglycolysis as a greener and more economically viable alternative to glycolysis, as part of the petrochemical glycol can be substituted with water, and the variety in end products is slightly reduced as primarily amines are formed.[35] However, a counterargument can be made: the absence of a split-phase in this process increases the energy demand for post-reaction product separation. While this may lower the energy input during depolymerization compared to hydrolysis, it also raises the likelihood of byproduct formation, thereby increasing the energy required for purification. For these reasons, hydroglycolysis has not yet been implemented at an industrial scale.[3]

Utilization and valorization of isocyanate-derived products: key considerations

Phosphorus-containing compounds. As previously mentioned, the resulting phosphorus-containing compounds can be utilized as flame retardants due to their smoke-reducing and corrosion-inhibiting properties. These components are particularly appealing because of their low smoke emissions and minimal toxicity.[31] A separate study indicates that when these phosphorus-containing compounds are treated with propylene oxide and subsequently blended, up to 15%, with virgin polyols and isocyanates, a rigid PU foam is formed. This foam demonstrates increased density, improved mechanical properties, and flame retardancy comparable to commercial products that rely on higher concentrations of conventional flame retardants[36] (see Scheme 11).

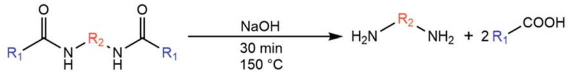
One notable observation across both valorization pathways is that the reaction products of phosphorolysis are not separated; instead, both the polyol and aromatic fractions are utilized in their entirety. Beyond the applications previously discussed, no additional uses for valorizing this fraction have been identified, and recent research in this area remains absent.

Amides/imides

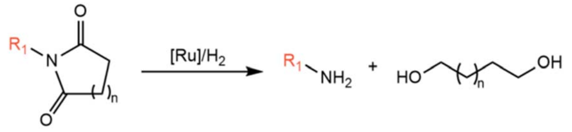
Amides are formed during acidolysis with organic acids. Depending on the type of PU foam used, these amides are typically acylated toluene diamine (TDA) or amidated methylenedianiline (MDA). According to the literature, amides containing unsaturated bonds, resulting from depolymerization with unsaturated dicarboxylic acids, can potentially be used as adhesives *via* radical polymerization. However, their reduced long-term stability due to acidity must be taken into account.[10]

Although this valorization pathway offers a potential solution for the aromatic fraction, it does not allow for reuse in PU synthesis, thereby rendering closed-loop recycling unfeasible. Moreover, only amides with double bonds are suitable for this application, and no literature confirms that these compounds are currently exploited in practice.

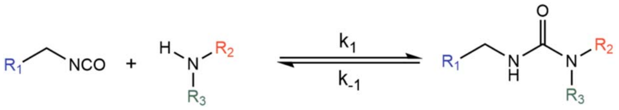
As an alternative, Liu *et al.* propose that amides can be converted into amines through hydrolysis using NaOH. These



Scheme 12 Hydrolysis of amides to amines using NaOH.



Scheme 13 Hydrogenation of cyclic imide to amine and diol.



Scheme 14 General reaction equilibrium of dynamic urea bonds with hindered structures.[38]

amines can then serve as precursors for isocyanates, enabling their incorporation into new PU formulations[37] (Scheme 12). However, this route requires an additional derivatization step, making it less attractive than recycling techniques that directly yield amines.

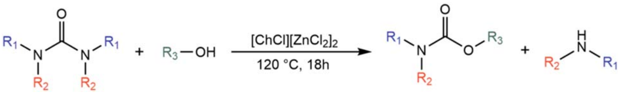
In the specific case where DCAs are used for acidolysis and cyclic imides are formed, these compounds can be readily converted into amines through a subsequent ruthenium-catalyzed hydrogenation or hydrolysis step (Scheme 13).[23,24]

Ureas

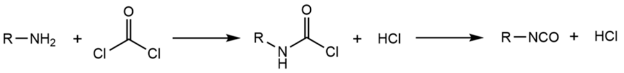
During aminolysis of PU, urea compounds are formed, which can undergo further polymerization to yield poly(urethane-urea) structures.[17] If these urea compounds are sterically hindered, meaning they possess bulky substituents on the nitrogen atom, they can also serve as dynamic polymers. These substituents disrupt the planarity of the amide bond, thereby destabilizing the urea linkage and enabling its dissociation under mild conditions into urea and isocyanate. When hindered urea bonds (HUBs) are incorporated into polymer synthesis, the resulting materials exhibit remarkable properties, including self-healing capabilities, recyclability, and shape-memory behavior (Scheme 14).[38]

A drawback of these techniques is that the direct synthesis of new polymers introduces limitations in terms of applicability, as different PU manufacturers have varying specifications depending on the intended application. Moreover, hindered urea bonds (HUBs) can only be formed if sterically hindered amines are used during aminolysis, amines that are inherently less reactive due to their steric bulk.

An alternative approach involves thermally cleaving the urea bond to regenerate isocyanates and amines. As previously discussed, urea bond formation is reversible, and upon heating, dissociation into isocyanate and amine can occur. In this process, the amine formed during aminolysis can be recovered, while the released isocyanate may be reused for PU synthesis.[39] However, a major challenge lies in the extremely high reactivity of isocyanates toward amines, approximately a thousand times greater than their reactivity toward primary aliphatic hydroxyl groups.[40] This leads to the rapid formation of highly stable urea compounds, stabilized by conjugation between the nitrogen lone pair and the π-electrons of the carbonyl group. Consequently, breaking the urea bond requires elevated dissociation temperatures, and the regenerated isocyanates tend to react immediately with available amines.



Scheme 15 Reaction of urea with alcohol to synthesize carbamates with the use of DESs.



Scheme 16 Phosgene process for the synthesis of isocyanates from amines.

Another valorization strategy for the urea fraction involves converting it into carbamate compounds *via* reaction with alcohols.[41] These carbamates can subsequently be transformed into isocyanates, as discussed in the section on carbamates. Additionally, recent research has explored the use of deep eutectic solvents (DESs), such as $[ChCl][ZnCl_2]_2$, to facilitate carbamate synthesis under relatively mild conditions, typically at 120 °C for 18 hours (Scheme 15). The use of DESs offers a more sustainable and economically viable process, as the catalytic system can be recycled with minimal loss of activity.[42]

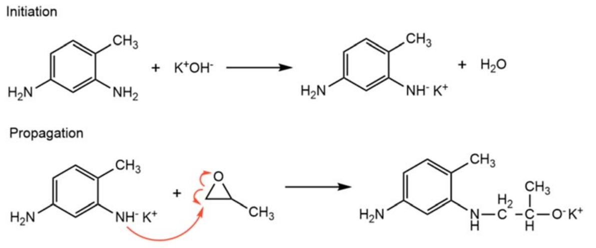
Amines

Since amines are among the most common end products and by-products of the chemical recycling of PU, a wide range of valorization strategies exists for this component. These approaches will be discussed in the following sections.

Formation of isocyanates. The predominant industrial method for producing isocyanates, covering all aromatic isocyanates and approximately 90% of aliphatic isocyanates, is phosgenation. This process entails the reaction of amines with phosgene to form isocyanates. Initially, an *N*-substituted carbamoyl chloride is formed in an exothermic reaction, which is subsequently followed by the elimination of hydrogen chloride at elevated temperatures (see Scheme 16).

Despite its widespread industrial use, the phosgenation process presents several challenges. The reaction is highly sensitive and requires precise control to prevent undesirable side reactions. One notable complication is the formation of insoluble amine hydrochlorides, which react slowly with phosgene and lead to reduced yields. Additionally the additives used in PU, the impurities at the end-of-life stage of PU,… all end up in the amine fraction and will react during the phosgene process.

Moreover, the process involves the handling of hazardous substances, including phosgene and hydrogen chloride, necessitating stringent safety protocols. Accurate management of reaction parameters, such as temperature, pressure, and



Scheme 17 Alkoxylation of TDA followed by propagation to form amine-initiated rigid polyols.

solvent selection, is essential to ensure the efficient production of the desired isocyanates.[43–45] These complexities suggest that incorporating recycled amines into the phosgenation process is impractical, primarily due to the extremely high purity requirements (in the ppb range). Additionally, compromising the operational stability of an isocyanate plant producing between 400 000 and 600 000 tonnes annually by introducing a few hundred tonnes of recycled amines is not considered feasible.[46] Purification of the amines can address this issue, for example through distillation. However, the additional purification costs significantly reduce the economic attractiveness of this route, making it difficult to compete with the price of virgin-grade amines.

An additional challenge for this pathway is that no new permits are being granted in Europe for the construction of phosgene plants. This implies that recycled amines, many of which are carcinogenic, would need to be transported to existing phosgene facilities for further processing. As discussed earlier, their processing is highly unlikely to be realized in practice.

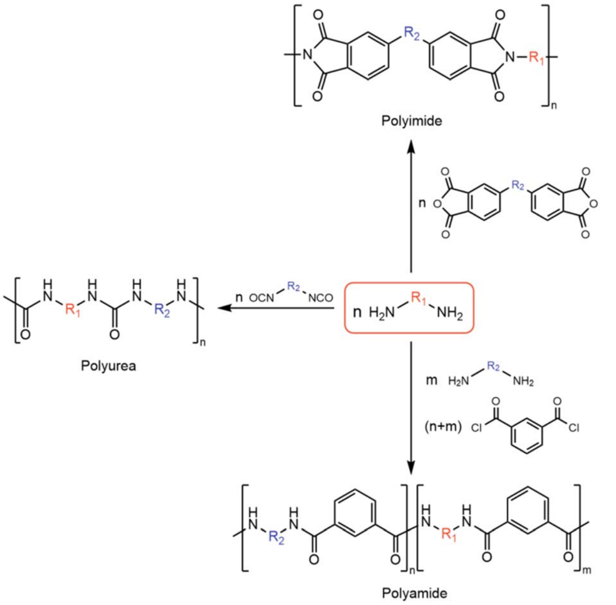
Given the limitations of conventional phosgenation, alternative non-phosgene routes have been explored. Although several processes have been developed for isocyanate synthesis, none are currently in commercial use.[47–49] One such method involves reacting amines with carbon dioxide in an aprotic organic solvent and a nitrogenous base to form the corresponding ammonium carbamate, which is then treated with a dehydrating agent. This approach has been applied to both aromatic and aliphatic isocyanates. The process relies on the efficient formation of amine–carbon dioxide salts, using acid halides such as phosphoryl chloride and thionyl chloride, as described by McGhee and Waldman in U.S. Patent 5,189,205, issued to Monsanto.[50]

Formation of rigid polyol. A high-functionality polyol used in rigid polyurethane (PU) and polyisocyanurate (PIR) foams, providing enhanced crosslinking, rigidity, and thermal stability, is referred to as a rigid polyol. Various processes have been developed to utilize amines as initiators in polyol synthesis. Given that most isocyanate derivatives possess an aromatic structure, particularly in the case of methylene diphenyl diisocyanate (MDI), which features a multifunctional configuration, the resulting polyols are predominantly applied as rigid polyols.

This concept has been substantiated in multiple scientific publications and patents. For example, Simon *et al.* demonstrated the reuse of toluene diamine (TDA), obtained from the glycolysis of flexible PU foams, as an initiator for the synthesis of rigid polyols (Scheme 17). The synthesis involved an alkoxylation reaction using propylene oxide and potassium hydroxide (KOH) as a catalyst. The reaction was carried out in a 2 L pressure vessel under an inert atmosphere at 120 °C and 3.5 bar. The residual catalyst was removed *via* ion exchange; however, at industrial scale, this purification step is typically performed through neutralization followed by filtration.[45] The amine-initiated polyol had a polydispersity index close to 1, which indicates a very narrow molecular weight distribution and therefore high uniformity of the polymer chains, and was successfully used in various cup foam tests, with up to 100% replacement of non-amine-initiated polyols.[36,51–54]

Amine derivatives sourced from isocyanates used in PU foam materials are commercially more expensive than alcohol-based initiators, which limits their broader industrial application. Furthermore, the alkoxylation process requires specialized infrastructure and stringent safety measures, as it involves highly exothermic reactions under pressure with reactive chemicals such as propylene oxide and strong bases like potassium hydroxide (KOH). These conditions present a hazard, defined as the inherent potential for harm, while the actual risk depends on the effectiveness of engineering controls and procedural safeguards.

As a result, it is unlikely that recycling facilities producing amines will possess in-house alkoxylation capabilities. Instead, the recovered amines would need to be transported to external alkoxylation facilities. This introduces a significant challenge: aromatic amines obtained from PU recycling are classified as hazardous and carcinogenic under the EU REACH regulation.[55] Their transport requires strict adherence to regulatory frameworks, including specialized packaging, proper labeling, licensed carriers, and extensive documentation. These



Scheme 18 Overview of polymerization reactions with amines to form polyimide, polyurea and polyamide.

requirements substantially increase both the cost and logistical complexity, rendering off-site alkoxylation economically and operationally unattractive.[56,57]

Formation of polymers–imide/amide/urea. Multifunctional amines derived from the recycling of rigid polyurethanes, can be used as a precursor for the synthesis of various polymers, including polyimides, polyamides and polyimines (Scheme 18).

Polyimides are high-performance materials known for their exceptional thermal stability, resisting temperatures above 500 °C, as well as their chemical resistance and outstanding dielectric properties, including high dielectric strength, low dielectric constant, and excellent electrical insulation. In addition, they exhibit remarkable mechanical toughness. These characteristics make polyimides suitable for a wide range of applications, such as insulating materials in cable wrapping, coatings in the paint industry, and components in aerospace engineering.

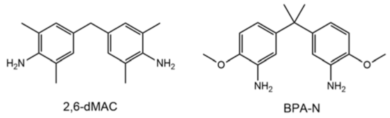
The most common synthesis route involves the reaction of diamines with dianhydrides, such as pyromellitic dianhydride, at elevated temperatures around 400 °C. This reaction leads to the formation of polyimide chains through a polycondensation mechanism.[58,59]

Given that most amines obtained from PU recycling are aromatic, the synthesis of aromatic polyamides, commonly known as aramids, represents a viable valorization pathway. These polymers are renowned for their heat resistance and strong fibrous properties, making them suitable for use in composites, films, boards, ropes, cables, and other high-performance applications.[60,61]

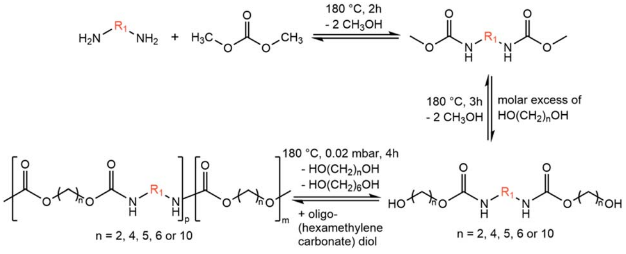
A notable example is provided by the study conducted by Hong *et al.*, in which poly(*m*-phenylene isophthalamide), an aramid related to the Kevlar® family, was successfully synthesized using 4,4′-methylenedianiline (MDA), isophthaloyl chloride (IPC), and *m*-phenylenediamine (MPD) as monomers.[62] The reaction mixture was stirred at 60 °C for one hour, after which $Ca(OH)_2$ was added and stirred for an additional 15 minutes during cooling to room temperature. The resulting polymer was subsequently washed and dried. The final product exhibited excellent flexibility and thermal stability, showing promising performance as a film material.[63]

Polyurea is synthesized through the reaction of an isocyanate with an amine, forming either a polymer or a pre-polymer. These materials have been extensively studied for their favorable mechanical properties, chemical resistance, and hydrolytic stability. Applications span a wide range of industries, including coatings, spray foams, and composite materials.[64–66]

An illustrative example is provided by Del Amo *et al.*, who valorized TDA obtained from the split-phase recycling of flexible PU foams. They successfully synthesized polyurea polymers by reacting various isocyanate compounds with TDA. Their study revealed that fully aromatic polyurea polymers exhibit lower melting temperatures compared to those containing aliphatic components, with a reduction from 218 °C to 170 °C. Despite this, the research demonstrated that valorizing the amine fraction into polyurea polymers is technically feasible. However, achieving optimal material properties requires careful selection of isocyanates whose functionality and molecular structure are compatible with the specific amine chemistry.[61]



Scheme 19 Chemical structure of 2,6-dMAC and BPA-N.

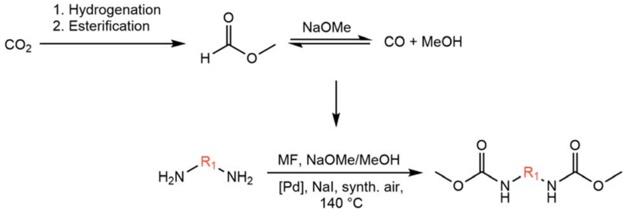


Scheme 20 Synthesis of non-isocyanate poly(carbonate-urethane)s.[69]

Valorization as a crosslinker in epoxy coatings. Epoxy resins, which form thermoset polymers, are renowned for their adhesive strength, mechanical robustness, and chemical resilience. These materials are extensively used in a wide range of applications, including electrical insulation, surface coatings, engineering composites, and structural adhesives. As a result, epoxy resins are frequently employed in the construction, automotive, aerospace, and marine sectors.

Amines represent one of the most important classes of curing agents for epoxy resins. The curing process involves the reaction of epoxy-functional molecules with amine groups, leading to the formation of a crosslinked polymer network. Both primary and secondary amines participate in this process *via* an addition reaction, whereby the epoxide ring is opened and a stable covalent bond is formed. Among these curing agents, 4,4′-methylenedianiline (MDA) is a widely used aromatic amine, valued for its ability to produce materials with exceptional chemical resistance and mechanical performance. MDA is particularly effective in applications requiring high thermal stability and resistance to aggressive chemical environments. For instance, MDA-cured epoxy resins are commonly used in protective coatings for pipelines, storage tanks, and industrial equipment exposed to harsh conditions. The curing process involving MDA can be accelerated by the use of catalysts such as boron trifluoride complexes or tertiary amines, which enhance reaction kinetics and reduce curing time.[67]

Basset *et al.* studied alternative monomers for MDA in epoxy resins due to their known toxicity. They found that MDA continues to deliver outstanding performance in terms of thermal stability, chemical resistance, mechanical durability, and overall strength, making it a preferred choice for highly demanding industrial applications. However, they have identified less toxic chemicals with somewhat worse properties, which may be suitable for less demanding applications[68] (Scheme 19).



Scheme 21 Synthesis of carbamates from amines using methyl formate.

NIPU materials. Non-isocyanate polyurethane (NIPU) presents a promising alternative material that can be synthesized from amines. Wołosz *et al.* were the first to report the successful synthesis of aliphatic–aromatic poly(carbonate-urethane)s exhibiting excellent mechanical properties (Scheme 20).[69]

Their work introduced a novel three-step route for producing non-isocyanate poly(carbonate-urethane)s. The first step involves the synthesis of alkylene or arylene bis(methyl carbamate)s from diamines, with both aliphatic and aromatic variants being investigated. In the second step, transurethanization is carried out to yield urethane diols. The final step consists of a polycondensation reaction between the urethane diols and oligocarbonate diols, resulting in the formation of the desired polymer.

The presence of pentamethylene moieties in the precursors of polyurethane hard and soft segments facilitates the efficient removal of diols during polymer synthesis and shortens the polycondensation time required to achieve high molar masses.

The synthesized non-isocyanate polyurethanes (NIPUs) demonstrated elevated thermal stability. Aliphatic NIPUs exhibited molar masses ranging from 7000 to 18 000 g mol^{-1}, with tensile strengths reaching up to 43 MPa and elongation at break values of up to 2000%. In comparison, aromatic NIPUs with similar molar masses and hard segment contents showed enhanced toughness but reduced flexibility.[70]

In light of the growing emphasis on sustainable materials, there has been a notable increase in recent publications focused on NIPUs, although their commercial adoption remains in its early stages. Several studies have highlighted the potential applications of NIPUs in adhesives, sealants, and coatings.[71] With continued research, it is anticipated that their use will expand into additional sectors.[72–75]

Carbamates. Various approaches have been developed for the synthesis of carbamates from amines. Ion *et al.* demonstrated a method in which aliphatic amines are converted into carbamates *via* reaction with carbon dioxide (CO_2) and various alcohols. Their study systematically explored a range of reaction parameters, including different types of amines and alcohols, as well as variations in temperature, molar ratios, and the use of dehydration agents. The researchers concluded that acceptable yields of carbamate formation can be achieved with the appropriate catalytic system. Notably, branched amines require the presence of a dehydration agent to facilitate the reaction, due to steric hindrance and reduced reactivity.[76]

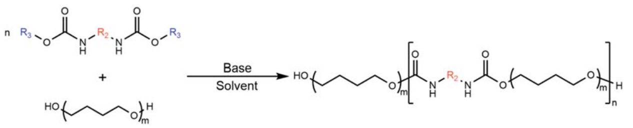
Hussong *et al.* successfully converted both TDA and MDA into carbamates. They performed an oxidative carbonylation reaction with the aforementioned amines using methyl formate (MF), which can be produced from CO_2 which, enables a green, non-phosgene route to polyurethanes (Scheme 21).

Although they have concluded three different pathways for side reactions to occur, they still showed promising results for further investigations into the design of selective catalysts.[77]

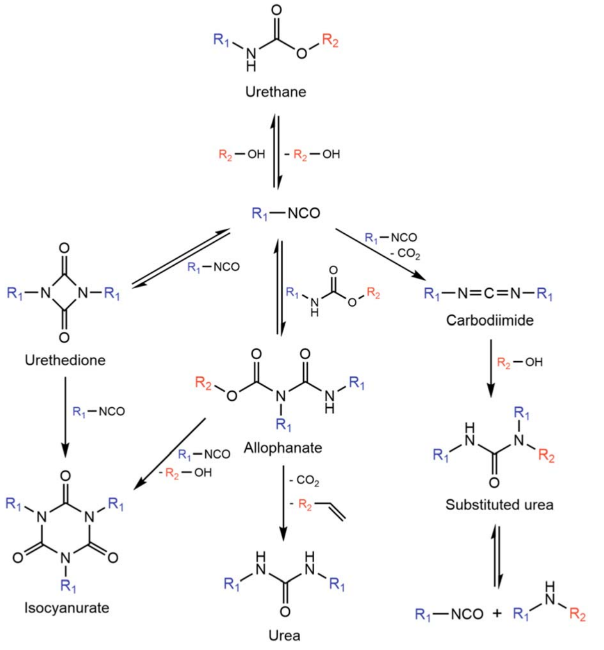
In summary, amines can be used to synthesize a wide variety of products. This offers multiple opportunities for valorization but also requires careful selection of recycling and upgrading strategies. The following sections will handle the valorization of carbamates after chemical recycling of PU.

Carbamates

A potential valorization pathway for carbamates was explored by Zahedifar *et al.*, who investigated the hydrolysis of the carbamate fraction to regenerate amines.[78] These amines could subsequently be converted back into isocyanates *via* the phosgenation process for use in new PU applications.[41] As previously discussed, this route presents several disadvantages, and it remains highly unlikely that recycled amines will be integrated into existing production facilities due to stringent purity requirements and operational constraints. An alternative approach was demonstrated by Zhao and Semetey, who showed that carbamates can be directly converted into polyurethane



Scheme 22 Synthesis of PU through transcarbamation of carbamates with polyols.



Scheme 23 Possible side reactions of isocyanates during the thermolysis reaction of carbamates. Based on the work of Prenveille *et al.*[87]

through transcarbamation with a polyol[79] (see Scheme 22). While this method enables the valorization of the carbamate fraction and the synthesis of "new" PU, it introduces limitations regarding the applicability of the resulting material. These limitations stem from the specific formulation requirements of different PU manufacturers, which may not be compatible with the properties of the synthesized PU.

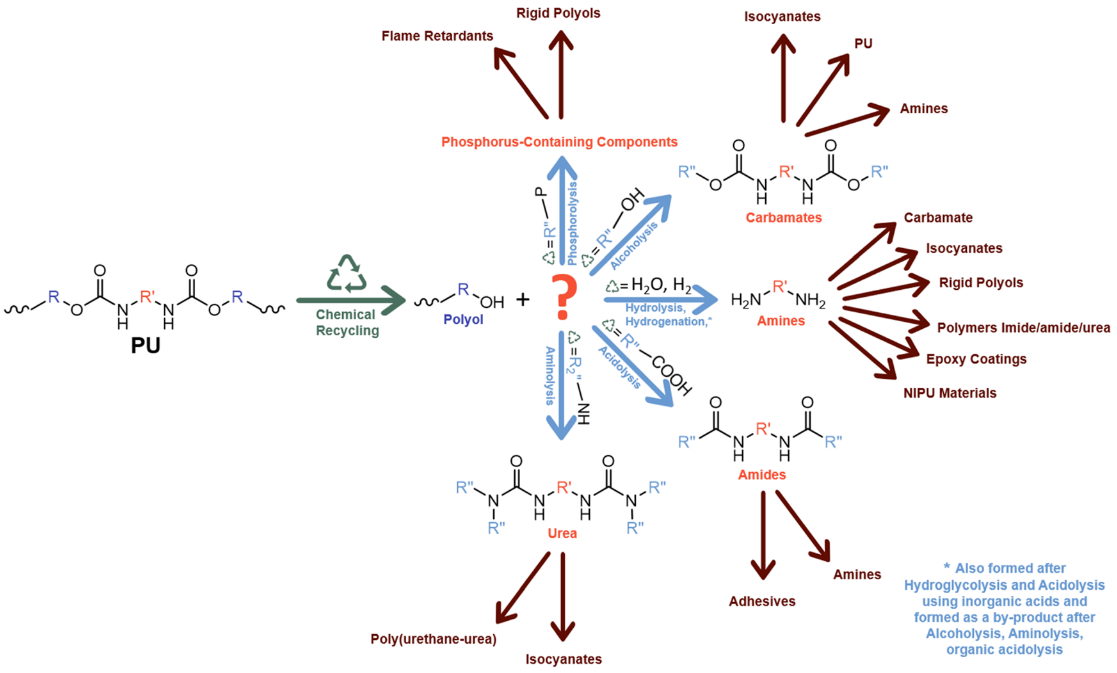
Nevertheless, this research provides a promising alternative route for the valorization of the carbamate fraction, contributing to the broader effort to develop sustainable and circular strategies for PU recycling.

A third valorization pathway involves the thermal dissociation of the urethane bond into an alcohol and an isocyanate. Similar to the urea bond, the urethane bond is thermally reversible. Due to the lower nucleophilicity of alcohols compared to amines, dissociation is more readily achieved for carbamates than for urea. The thermal decomposition of carbamates has been extensively documented in the literature as a phosgene-free route for isocyanate production.[47,80–85] This method offers a more sustainable and safer alternative to conventional phosgenation. However, several challenges remain, including the identification of efficient catalysts and the optimization of reaction conditions to suppress unwanted side reactions. Despite significant progress in recent years, with reported yields ranging from 85% to 95%, thermolysis has not yet been adopted at an industrial scale.[41,86] One key barrier is the limited understanding of the side reactions that occur during thermolysis and the lack of effective strategies to mitigate them. As illustrated in Scheme 23, various side reactions may take place, particularly when bifunctional isocyanates or alcohols are present. These by-products can undergo further polymerization, leading to the formation of oligomers, which complicates product purification and process control.

Most of these reactions are conducted at temperatures ranging from 150 °C to 300 °C in high-boiling, inert solvents and in the presence of a catalyst. Commonly used solvents include higher alkanes, arenes, ethers, esters, and ionic liquids.[47] A wide variety of catalysts have been explored for this process, including metals, metal oxides, metal complexes, salts, organometallic compounds, and more specialized systems such as montmorillonite K-10 (ref. 41) and ionic liquids.[88,89] The structure of the alcohol used during the chemical recycling of polyurethane also has a significant influence on the subsequent thermolysis reaction. Nees *et al.* showed that the use of mono-alcohols is essential to prevent further polymerization between the alcohol and diisocyanate, which would otherwise lead to the re-formation of polyurethane during thermolysis. In addition, alcohols with sufficiently low boiling points and secondary alcohols were found to be advantageous for the thermolysis process.[90]

The thermolysis method offers a relatively straightforward route to recover isocyanates directly from carbamates formed during the alcoholysis of polyurethane (PU) waste. Notably, the complete process, from PU waste to the valorization of the isocyanate fraction *via* carbamate thermolysis, has been successfully demonstrated.[90] At present, this is the only tested pathway capable of reverting waste PU back to its original building blocks, representing a significant step toward closed-loop recycling in polyurethane chemistry.

All chemical recycling pathways and their subsequent valorization routes can be summarized as shown in Fig. 3. The figure offers a consolidated overview of the major steps involved, from depolymerization to the formation of value-added intermediates, providing a clear outline of the possible processing routes.



* Also formed after Hydroglycolysis and Acidolysis using inorganic acids and formed as a by-product after Alcoholysis, Aminolysis, organic acidolysis

Fig. 3 Overview of chemical recycling techniques of PU, their corresponding end products and their valorization pathways.

Industrialization criteria

As outlined in previous chapters, numerous valorization opportunities exist for the aromatic fraction obtained from PU recycling. However, not all pathways are equally sustainable, economically viable, or technically feasible. Therefore, only a selected number of specific valorization routes will be discussed and assessed based on their actual industrialization potential. This initial selection was made using the following criteria: a minimum Technology Readiness Level (TRL ≥ 3) of the chemical recycling process, a limited number of reaction steps (no more than one valorization step following the chemical recycling process), and a realistic likelihood of implementation (*e.g.*, recycled amines will not be used in existing phosgene plants). Based on these criteria, only a few valorization pathways remain eligible and will be evaluated in terms of circularity, energy demand, and the use of co-reagents, catalysts, and solvents (Fig. 4).

One promising circular pathway is the valorization of urea compounds into poly(urethane-urea)s. These materials are recyclable, and the presence of hindered urea bonds (HUBs) enhances circularity by enabling reversible dissociation and reformation. This allows for repeated reprocessing with minimal material loss. The energy demand for poly(urethane-urea) synthesis is relatively low, as highly reactive isocyanates can react under ambient conditions. However, the use of such isocyanates presents a significant drawback due to their inherent toxicity and associated safety and environmental concerns.

Another valorization route involves the thermal dissociation of urea bonds to regenerate isocyanates and amines. This pathway offers strong circularity potential, as the recovered isocyanates can be reused in PU synthesis, while the amines can be recycled for aminolysis. Energetically, however, this process is less favorable: the high reactivity of isocyanates toward amines necessitates harsh deblocking conditions, typically in the range of 350–450 °C.[40] Thermolysis conditions can be moderated by employing secondary, tertiary, or aromatic amines. However, these are rarely used in PU aminolysis due to their lower reactivity and, in the case of aromatic amines, their classification as carcinogenic substances. A reduction in deblocking temperature can also be achieved by using large quantities of solvent (1–10 wt% urea), though this introduces economic and sustainability drawbacks. On the other hand, the process does not rely on toxic or expensive catalysts, which is a distinct advantage compared to many alternative recycling strategies.

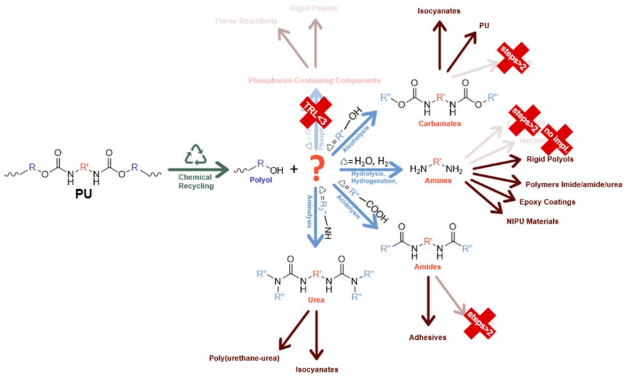


Fig. 4 Overview of chemical recycling techniques of PU, their corresponding end products and their valorization pathways with restrictions.

The synthesis of rigid polyols from amines offers a promising circular pathway, as the resulting PU materials are recyclable. From an energetic standpoint, the alkoxylation process is favorable: the reaction with propylene oxide is strongly exothermic and does not require external energy input. The main drawback lies in safety concerns, as the process operates under elevated pressure and involves highly reactive chemicals such as propylene oxide and strong bases like KOH. Although the absence of precious metal catalysts is beneficial, the need to remove residual KOH introduces additional operational costs.

The use of amines as curing agents for epoxy coatings is less favorable in terms of circularity, as these coatings are not recovered or recycled at end-of-life. Energetically, however, this pathway is highly advantageous: the curing reaction proceeds at room temperature, followed by a short post-curing step at 80 °C for two hours.[91] Moreover, epoxy resins and their common additives are generally non-toxic and commercially available at low cost, making this application economically accessible despite its limited circular potential.

The synthesis of polyimides from amines requires expensive aromatic dianhydrides and involves an energy-intensive imidization process. Although polyimides exhibit excellent thermal and mechanical properties, these very characteristics pose a significant drawback for recyclability. Their high thermal stability and strong intermolecular bonding make them highly resistant to chemical or thermal degradation, thereby limiting the effectiveness of conventional recycling strategies.

In contrast, the polyamide pathway is more favorable in terms of energy demand and reagent accessibility, due to large-scale production and the use of relatively inexpensive diacids. As thermoplastics, polyamides are readily recyclable, which enhances their circularity. Polyurea stands out for its rapid, energy-efficient, and solvent-free polymerization. However, its sustainability is undermined by the use of phosgene-based isocyanates and its limited recyclability.

The conversion of amines into non-isocyanate polyurethanes (NIPUs) represents a promising valorization route, enabling the development of closed-loop recycling systems. Nevertheless, this pathway is associated with several drawbacks: the required reagents are relatively expensive, and the overall synthesis is considerably more energy-intensive than conventional PU production.

It is important to note that across all these derivatization routes, many of the aromatic amines employed are classified as carcinogenic. Within the European Union, their use and transport are strictly regulated under the REACH framework. This regulatory burden complicates the logistics of transferring such intermediates from recycling facilities to valorization sites. As a result, safety and regulatory considerations must be integrated into any realistic assessment of the economic and practical viability of amine-based polymer production.

Table 2 Overview of the valorization pathways with their corresponding relative energy demand, circularity, closed loop recycling and the use of toxic/dangerous reagents

Valorization route	Toxic/dangerous reagents used	Energy demand	Circularity of the end product	Closed loop
Urea to HUBs	Isocyanates	Low	Recyclable	No
Urea to isocyanates	—	High	Recyclable	Yes
Amines to rigid polyols	Propylene oxide, KOH	Low	Recyclable	Yes
Amines to polyurea	Isocyanates	Low	Limited recyclability	No
Amines to polyimides	—	High	Recyclable	No
Amines to polyamides	—	Low	Recyclable	No
Amines to epoxy coatings	—	Low	Not recyclable	No
Amines to NIPU's	—	High	Recyclable	Yes
Carbamates to PU	Toluene	High	Recyclable	Yes
Carbamates to isocyanates	—	High	Recyclable	Yes

The valorization of carbamates into PU *via* transcarbamation can be considered a promising pathway in terms of circularity. However, this method requires a polycondensation reaction at 130 °C for 16 hours, which is relatively energy-intensive compared to the exothermic nature of standard PU synthesis. Additionally, the repolymerization process involves solvents such as toluene and has been reported to yield only around 50%, which is far from optimal.

From both an economic and sustainability perspective, the thermal dissociation of carbamate bonds into alcohols and isocyanates presents opportunities as well as challenges. The requirement for high-boiling inert solvents and elevated reaction temperatures (150–300 °C) implies significant energy input, which may limit the feasibility of large-scale implementation. Furthermore, the need for specialized catalysts, some of which are costly or difficult to recycle, affects both the sustainability and cost-efficiency of the process. In terms of circularity, however, this valorization method is highly promising, as it enables the recovery of PU building blocks and the alcohol used during alcoholysis. Additionally, the process does not rely on toxic or expensive catalysts or solvents.

Conclusion

Although the valorization of the isocyanate-derived fraction from PU recycling has long been overlooked, recent advancements have led to the development and investigation of several promising pathways. While many of these routes remain largely theoretical and face considerable practical or economic barriers, some have demonstrated genuine industrial relevance and applicability.

Table 2 provides an overview of the different valorization options, including their energy requirements, the use of potentially hazardous or toxic reagents, the degree of circularity achieved in the final product and whether the final product obtained after valorization can be reused in the synthesis of polyurethane, thereby enabling the creation of a closed-loop recycling system. Assigning precise numerical values to each of these criteria is, however, not feasible due to the large variability. This variability arises from: (1) the recycled PU itself, polyurethanes can be synthesized from numerous combinations of polyols and isocyanates, leading to a wide range of possible PU compositions and corresponding recyclates; and (2) the recycling process and subsequent valorization steps. For example, in alcoholysis, multiple types of alcohols can be employed. This not only broadens the diversity of possible alcoholysis products but also affects the valorization of the resulting carbamates, since the alcohol becomes incorporated into the carbamate structure through a transcarbamoylation reaction.

Consequently, we provide only relative assessments of these three parameters, offering an initial indication and enabling comparison between the various valorization strategies. As noted earlier, the choice of the specific recycling pathway, and of the particular molecules involved, has a substantial influence on the overall process. For all valorization strategies, the technology readiness level (TRL) remains below 6, as they are still in the research phase. As a consequence, comparing these strategies on the basis of TRL does not provide meaningful insight.

As can be seen from Table 2, several recycling and valorization pathways emerge as particularly promising according to the defined criteria. These include the conversion of amines into rigid polyols, the synthesis of polyamides from amines, the production of non-isocyanate polyurethanes (NIPUs) from amines, and the thermolysis of ureas and carbamates to regenerate isocyanates. However, not all criteria carry equal weight. Currently, there is a strong emphasis on achieving closed-loop recycling systems, which makes the amine-to-polyamide route less attractive, as it does not enable direct reuse in polyurethane synthesis.

This leaves valorization routes toward rigid polyols, NIPUs, and regenerated isocyanates as the most relevant options. As discussed earlier, the thermolysis of urea compounds is significantly more complex than that of carbamates, which further reduces the appeal of this pathway. Based on the relative assessment of the selected criteria, the most viable valorization strategies for the derivatized isocyanate fraction therefore appear to be the conversion of amines into rigid polyols and NIPUs, as well as the thermolysis of carbamates to reform isocyanates.

For the synthesis of rigid polyols and NIPUs from amines, future research should consider whether these compounds need to be protected or otherwise handled carefully after recycling and during transport to comply with restrictive REACH regulations. Additionally for the valorization of amines into rigid polyols, it is important to explore methods that avoid the use of KOH and propylene oxide, in order to improve process safety. For the synthesis of isocyanates *via* the thermolysis of carbamates, attention could be given to developing more efficient catalysts and solvents to reduce the reaction's energy requirements and minimize by-product formation.

Ultimately, however, the selection of a suitable valorization pathway involves trade-offs among technical feasibility, economic viability, environmental impact, and regulatory constraints. A case-specific evaluation is essential to determine the most appropriate strategy for each PU recycling scenario.

Author contributions

Marthe Nees: writing – review & editing, writing – original draft, visualization, validation, conceptualization. Matthew Porters: writing – review & editing, writing – original draft. Muhammad Adeel: writing – review & editing, writing – original draft. Lukasz Pazdur: writing – review & editing, validation, supervision. Christophe M. L. Vande Velde: writing – review & editing, validation, supervision, resources. Pieter Billen: writing – review & editing, validation, supervision, resources.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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